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M.H.

Den 20sten November is na een kortdurende ziekte

WILLEM DE SITTER

overleden. Zijn heengaan beteekent een zeer zwaar verlies voor de wetenschap in het algemeen, voor de Sterrekunde en voor onze afdeeling in het bijzonder.

DE SITTER studeerde te Groningen aanvankelijk in de wiskunde maar onder invloed van J. C. KAPTEYN en van diens vriend Sir DAVID GILL, directeur van de Cape Observatory, die het Groningsch sterrenkundig laboratorium in October 1896 bezocht, wendde hij zich tot de sterrekunde. In volge een verzoek van Sir DAVID GILL om te Kaapstad de daar verrichte heliometer-waarnemingen van de wachters van Jupiter te reduceeren, ging DE SITTER, na doctoraal examen in de wis- en sterrenkunde te hebben afgelegd, naar Kaapstad, waar hij gedurende twee jaar werkzaam bleef, een verblijf, dat in menig opzicht beslissend voor zijn leven zou zijn. Hier werd zijn aandacht gevestigd op vraagstukken in verband met de Jupiter satellieten; problemen, die hem nooit meer hebben losgelaten.

Welk een uitstekend werk DE SITTER op dit gebied geleverd heeft, blijkt uit het schitterend getuigenis, dat de president van de „Royal astronomical Society" Dr. CROMMELIN hieromtrent aflegde toen in 1931 de aan DE SITTER toegekende Gold Medal of the Society werd uitgereikt, een onderscheiding, die gewoonlijk als de hoogste op astronomisch gebied wordt beschouwd.

Teruggekeerd in het vaderland werd hij assistent aan het Sterrenkundig laboratorium te Groningen en promoveerde op een proefschrift getiteld „Discussion of Heliometer observations of Jupiter Satellites", waarin resultaten van zijn werk te Kaapstad waren neergelegd.

Te Groningen verrichtte hij veel uitmuntend werk o.a. over de bepaling van z.g. „eigen bewegingen" der vaste sterren, parallaxen en photometrie.

In 1908 werd DE SITTER tot hoogleeraar in de sterrekunde te Leiden benoemd, in 1918 tot Directeur van de Sterrewacht.

DE SITTER heeft, ondanks zijn niet sterke constitutie, op wetenschappelijk gebied enorm veel gepraesteerd, naast zijn reeds vermeld levenswerk over de manen van Jupiter, vestigde hij zijn aandacht op verschillende problemen, waarvan slechts enkele aangehaald kunnen worden. Een zijner wenschen ging uit naar het maken van een samenhangend systeem van de astronomische constanten zooals de precessie en de nutatieconstanten, de lengte van het jaar, de straal van de aarde, de afplatting der aarde, de afstand en de massa van de maan enz.

Bij het derde eeuwfeest der Leidsche Sterrewacht, tevens het zilveren Hoogleeraarschap van DE SITTER, wees VENING MEINESZ er nog op van hoeveel belang dit werk voor de geodeten is.

Het meest heeft wel tot de groote internationale bekendheid van DE SITTER bijgedragen de wijze waarop hij EINSTEIN's relativiteitstheorie in de astronomie heeft toegepast en uitgebreid. Uit zijn beschouwingen hierover is geboren zijn, van EINSTEIN's opvattingen afwijkende, conceptie van het heelal, welke door de astronomen veelal betiteld wordt met den naam: „DE SITTER's Universe". In dit bijna geheel ledig treden bewegingen op met enorme snelheden, hetgeen in waarnemingen, verricht aan het Mount Wilson observatory, bevestiging heeft gevonden. Later werd deze opvatting door DE SITTER gewijzigd en uitgebreid tot de theorie van het uitdijend heelal.

Hoezeer deze arbeid door zijn vakgenooten op prijs wordt gesteld, blijkt eveneens uit de woorden van den voorzitter van de Royal astronomical Society; de gouden medaille toch was toegekend op grond van DE SITTER's „Theoretical investigations on the orbits of the satellites of Jupiter and for his contributions to the Theory of Relativity".

Wordt in dit uit den aard der zaak zeer onvolledig overzicht reeds getoond, dat DE SITTER ondanks zijn wankele gezondheid op wetenschappelijk gebied een hoeveelheid werk heeft mogen verrichten meer dan voldoende om het geheele leven van een geleerde te vullen, des te grooter is onze bewondering voor DE SITTER's enorme werkkracht, als wij bedenken, hoeveel hij op geheel ander gebied heeft kunnen verrichten. Slechts zelden komt het voor, dat een dergelijk geleerde tegelijk is een man van de daad en een goed organisator; DE SITTER was ook op dit gebied een onvolprezen meester, hij was, zooals een zijner leerlingen het uitdrukte, een geboren bestuurder.

Het is hem vergund geweest om de Leidsche Sterrewacht opnieuw te organiseeren en ook al maakten de zoo ongunstige

tijdsomstandigheden, dat zijn met KAPTEYN uitgewerkte verstrekkende plannen niet geheel volledig konden worden uitgevoerd, toch is het hem met zijn medewerkers, waaronder vooral HERTZPRUNG genoemd moet worden, mogen gelukken de Leidsche Sterrewacht opnieuw te maken tot een inrichting volkomen op de hoogte van den tijd en haar wederom een eereplaats te doen innemen onder de eerste sterrewachten der wereld. Een astrophysische en een theoretische afdeeling werden eraan toegevoegd, zoodat een schitterend geheel werd verkregen, terwijl de universeele belangstelling van DE SITTER in alles wat zijn vak betrof ervoor waakte, dat aan een der deelen, ook die niet onmiddellijk met zijn eigen werk samenhingen, te kort werd gedaan.

Zijn organisatiegeest breidde de werkingsspheer van de Leidsche Sterrewacht uit tot in Zuid-Afrika door de bekende samenwerking met Johannesburg, waar sinds dien tijd steeds een der Leidsche astronomen werkzaam was.

Hoezeer DE SITTER zich ook met de meest fundamenteele problemen van de astronomie bezighield, blijkt wel uit de wijze waarop hij met hart en ziel medewerkte aan de organisatie der Leidsche expeditie naar Keneya in Centraal Afrika, welke gericht was op het verkrijgen van een beter systeem van de posities der vaste sterren, een onderneming, die met DE SITTER's eigen werk weinig verband hield en waarvan de goede vruchten pas in de toekomst geplukt zullen kunnen worden.

Het was teekenend voor den invloed zijner persoonlijkheid hoe deze niet welsprekende man steeds autoriteiten en begunstigers der wetenschap voor de belangen der sterrekunde wist te interesseeren. Steeds voelde men, dat het hem altijd alleen te doen was om het belang der zaak, nooit om het bereiken van eigen voordeel of ter voldoening van persoonlijke ijdelheid, die hem vreemd was.

De ROCKEFELLER Foundation zegde hem ruim honderdduizend dollar toe voor het bouwen en exploiteeren van een grooten kijker in een eigen gebouw te Johannesburg; jammer genoeg heeft DE SITTER de verzending van het instrument niet meer mogen beleven.

DE SITTER heeft het uitmuntend verstaan medewerkers te kiezen en te behouden. Hij stelde in hen zulk een vertrouwen, dat hij hun algeheele vrijheid liet in den opzet en de uitvoering van hun werk, echter altijd voeling met hen houdend en steeds bereid hen met raad en daad bij te staan. Hij bezat de kostbare gave om van zijn medewerkers zijn vrienden te maken.

De organisatorische talenten van DE SITTER bleven ook in het buitenland niet onopgemerkt, met het gevolg, dat men hem van 1925—1928 de moeilijke taak toevertrouwde van voorzitter der Internationale astronomische Unie in een tijdperk van groote moeilijkheden. Ook zijn leiding van het Internationaal Astronomisch Congres te Leiden werd een groot succes.

Aan eerbewijzen heeft het DE SITTER voorzeker niet ontbroken ; eeredoctoraten, eerelidmaatschappen, medailles werden in groote getale zijn deel.

Van onze Akademie was DE SITTER sedert 1912 een getrouw lid, zelden ontbrak hij op de vergadering, gaarne nam hij aan de discussies deel, menigvuldig waren de voordrachten, die hij hield en wij allen zullen ons zijner herinneren, zooals hij dan voor ons stond sprekend op zijn ietwat hortende, schijnbaar nonchalante wijze, waarbij hij echter altijd zijn gehoor wist te boeien. Ook hier toonde hij zich weer de eenvoudige, altijd bereidwillige persoon, die steeds gereed was in te springen om een spreekbeurt te vervullen ; nog op de laatste onzer vergaderingen, die hij mocht beleven, hield hij op verzoek van het Bestuur een voordracht.

Zoo hebben wij DE SITTER in zijn volle persoonlijkheid leeren kennen en leeren apprecieeren en wij mogen verklaren, dat met DE SITTER is heengegaan een groot geleerde, een uitmuntend organisator, een nobel mensch, een vriend van velen, een navolgingswaardig voorbeeld voor allen.

Geophysics. — *On the relation between microseisms and depressions in Western-Europe and on the Ocean.* By S. W. VISSER. (Communicated by Prof. Dr. E. VAN EVERDINGEN Jr.).

(Communicated at the meeting of November 24, 1934).

§ 1. At the assembly of the International Seismological Association at Manchester in 1911 E. VAN EVERDINGEN [1]) has presented some preliminary results of a research by G. VAN DIJK into the correlation of microseismic movements at De Bilt and the sea waves in Western Europe. Each part of the moving sea appears to generate a group of well defined periods: the North Sea being agitated, often very strong waves with a period of 3.5 sec are visible, rough sea on the coasts of Scotland gives a period of 5 sec, on the coasts of Norway 6 sec, in the Atlantic 7 sec.

As a matter of fact the microseisms at De Bilt are controlled daily on behalf of the weather forecast, because their character may reveal the presence of a remote depression in the Atlantic. Especially during the war, when the daily weather reports were wanting, this method often proved to be trustworthy.

GUTENBERG a.o. [2]) have concluded to a close connexion between microseisms in Europe and the state of the sea especially on the coast of Norway. TAMS has found a correlation of 0.88 between the microseisms at Hamburg and the surf at the Norwegian coasts [3]).

GHERZI [4]) has stated that cyclones passing at very great distances procure heavy microseisms at Zi-Ka-Wei, but a rough sea at the coasts of China is rather inactive. LEE, according to a recent publication of WHIPPLE [5]), demonstrates that "the occurrence of a well developed depression over the eastern half of the North Atlantic is a necessary but not a sufficient condition for the development of microseisms".

The results of GHERZI and LEE and the old experience at De Bilt clearly point in the same direction concerning the cause of microseisms. At the request of Prof. VAN EVERDINGEN I have investigated this problem. The present paper records the preliminary results.

§ 2. At De Bilt the microseismic character of the Wiechert seismograms has been read daily from April 1908 up to this day. The amplitude and the period of the Galitzin seismograms have been measured daily at 6 h G.M.T. from January 1, 1917, to December 31, 1929, moreover during January, 1930, at 1 h, 7 h, 13 h and 18 h. We have studied the Galitzin readings especially from 1925.

§ 3. When comparing microseisms with atmospheric pressure we are often struck by a close resemblance in their range. Fig. 1 represents both phenomena for January 1930. Good concordance is present for the period of January 3—14. Though this effect is not always present, it often points to a relation of microseisms with atmospheric pressure rather than with the state of the sea.

The state of the atmosphere in Western Europe is rather chaotic. As

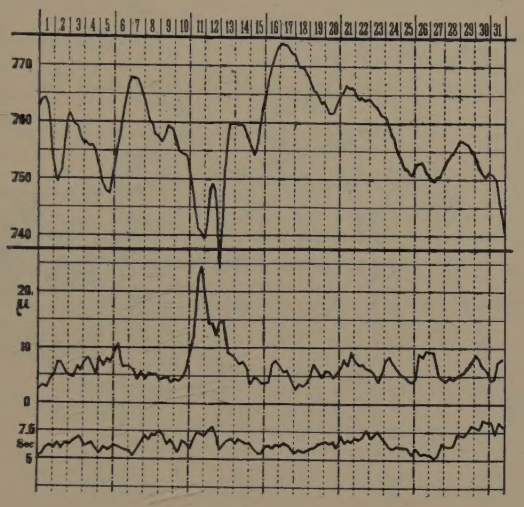

Fig. 1. Atmospheric pressure and microseisms at De Bilt, January 1930. Pressure in mm; amplitude in μ, period in seconds.

a rule two or more depressions or a sequence of secondaries are simultaneously active and disturbing each others microseismic effects. Therefore in order to detect some relation it is absolutely necessary to select well isolated, solitary depressions.

§ 4. We have sifted out the depressions by means of the cyclone tracks in the monthly weather review of De Bilt and controlled and extended them to the west with the aid of the circumpolar weather maps of Hamburg (Deutsche Seewarte). We have bestowed much care on this part of the research, because all conclusions depend upon the reliability of the cyclone tracks selected.

In this manner we found during the period 1925—January 1930 about 50 cases, in which strong microseisms at De Bilt were obviously related to well defined cyclones in the N-E Atlantic Ocean and Western Europe.

The map, fig. 2, contains the positions of the depression centres at the moment of maximum microseisms at De Bilt. We learn from this map that the maximum microseismic effect is by no means clearly connected with the coastal regions affected by the cyclones. The spots are spread at random in the field of observation. One feature, however, is evident:

a fairly great number of depressions generates microseisms when at a rather great distance in the Atlantic Ocean. This is a first indication that the typhoon effect of the Far East is present for the cyclones of our regions too.

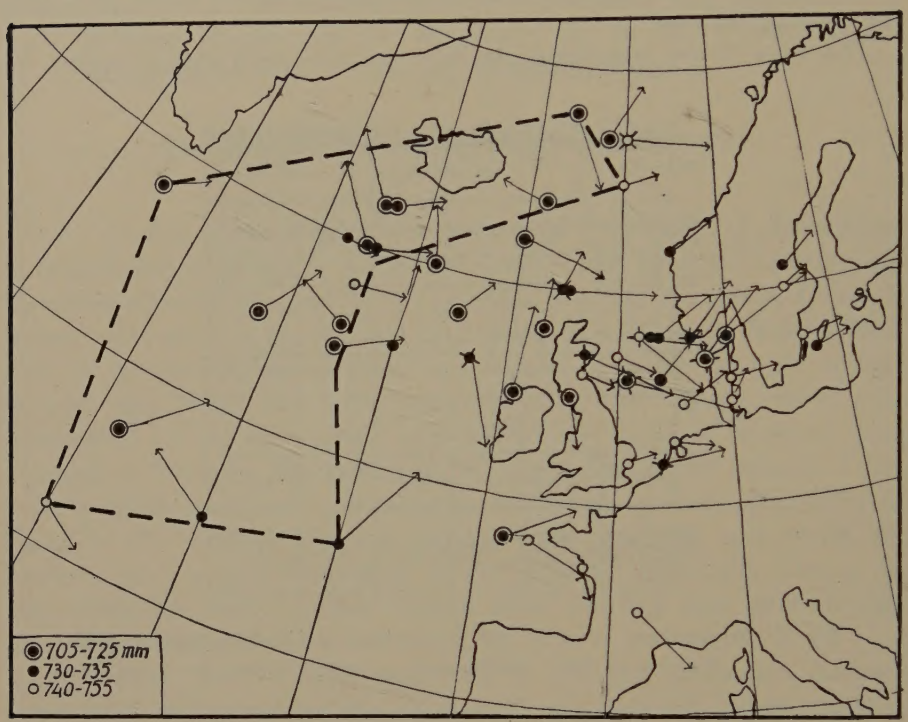

Fig. 2. Cyclone centres and microseisms.

§ 5. The next step was investigating the state of the sea. For this purpose during each period of strong microseisms the state of the sea was read from the Hamburg and the De Bilt daily weather maps for seven coastal regions, viz. *I* Ireland, *S* Scotland, *N* Norway, *D* Danmark, *H* Holland, *K* the Channel, *B* the Bay of Biskaya, *O* the Baltic. Generally rough sea and microseisms coincide, but obvious exceptions are present. In a number of cases the state of the sea even shows a minimum whilst microseisms have maximum values. The following data may serve as examples. (Table I).

The depressions connected with such cases are situated (with only one exception, viz. the centre in N-W Ireland) at great distances, within the area limited by a broken line in fig. 2.

We have found herewith an obvious indication that GHERZI's typhoon effect is also present in Western Europe. It is, however, a rather rare phenomenon, the weather features being much more complicated than in the Far Eastern seas.

TABLE I.

Date	Micros (N + E) : 2	State of the sea *)							
		I	*S*	*N*	*D*	*H*	*K*	*B*	*O*
Dec. 1925									
6	4.8	4—7	0—2	**5—7**	**4—5**	1—2	(6)	—	**5—6**
7	**8.4**	4	0—5	4—6	1—2	0—1	0—6	(6)	1—3
8	4.7	**6—7**	**6—7**	4—5	2—4	1—2	2—6	(4)	**2—4**
9	5.2	**4—9**	3—5	**4—6**	**2—6**	**1—4**	**3—7**	(3)	2—3
Dec. 1926									
7	4.6	0—5	0—5	3—5	3—4	0—1	0—2	2—4	1—3
8	**10.8**	0—6	(4)	4	1—4	0—1	0—3	2—4	1—2
9	5.6	1—6	(6)	**4—6**	**2—4**	1	0—1	**2—5**	**4—5**
10	4.4	**4—6**	0—4	**4—6**	1—5	0—1	0—1	3	2—4
Dec. 1927									
18	5.8	3—7	(0)	1—3	**3—4**	0	(7)	1—5	**2—6**
19	**14.3**	3—4	(1)	2—3	2	0—1	0—7	(1)	1—6
20	7.6	(7)	0—2	2—3	2—3	0—1	**2—8**	(5)	2—3
21	4.8	(6)	**3—6**	2—3	2—4	0—2	4—6	(3)	0—2

*) in brackets incomplete data of one record only.

§ 6. We have to do with depressions ranging from 705 to 755 mm and may expect therefore great differences in their effects upon microseisms. Indeed we find an obvious decrease of the amplitude with increasing pressure in the cyclone centre.

TABLE II.

Pressure	711	720	725	730	735	740	749
Amplitude (N + E) : 2	10.4	8.5	9.8	10.6	7.8	6.0	7.3
V	5.0	4.4	4.3	4.4	3.2	2.8	3.0
Period (N + E + V) : 3	7.0	7.2	6.4	6.3	6.2	5.1	5.6

A similar decrease of the period appears to exist. The map, however, teaches us that the deeper depressions are as a rule the farther off ones and therefore this feature of the period may be due to the distance.

As to the distance the amplitude does not show an evident effect (fig. 3*a*). Here again we find the deepest depressions generating the strongest microseisms.

The periods are clearly increasing with increasing distance, especially for the deep depressions of 705—725 mm (fig. 3*b*), being in general the

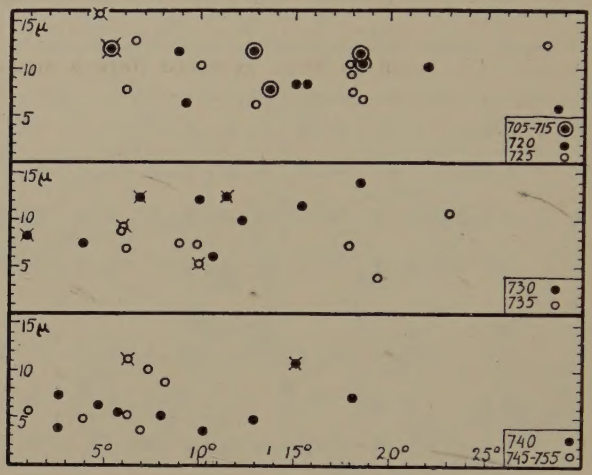

Fig. 3*a*. Amplitude and distance.

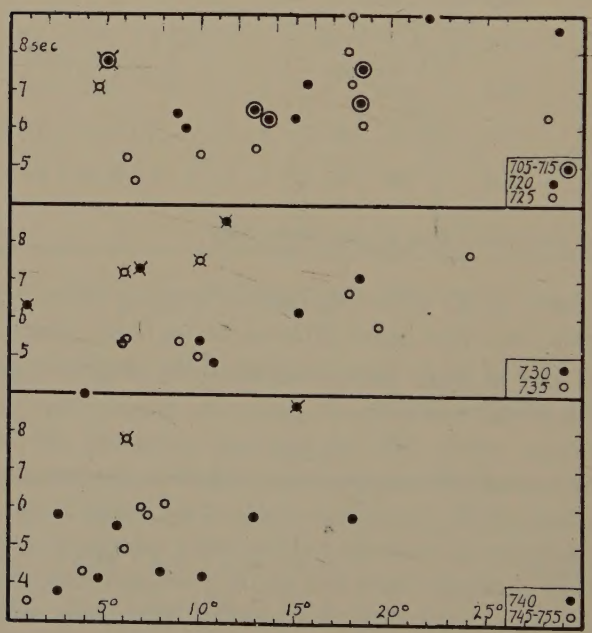

Fig. 3*b*. Amplitude and period.

remote Atlantic cases. Indeed we may conclude that the result for the period in table II is influenced by the distance.

As to the smaller depressions situated as a rule in or near to the continent, local influences are probably disturbing the developing of the distance effect.

In fig. 3*b* we find in the upper left hand corners of the diagrams some

obvious exceptions of the distance rule, nine in total and marked by a cross. These nine cases are marked by a cross in the map also and we see that seven of them are situated in a narrow region from Scotland to Denmark. They are characterized by a much larger period than concords with their distance. We seem to have detected here a special system of microseisms, but it is not yet possible to say something more of these "North Sea Microseisms".

§ 7. The microseisms appear to depend upon the direction of the cyclone tracks. We have indicated this direction at each cyclone centre of the map (fig. 2); the length of the line is corresponding with the amplitude of the microseisms at De Bilt.

We have plotted these directions in the vector-diagrams of fig. 4. The vertical arrow represents the direction towards De Bilt, whilst the distance

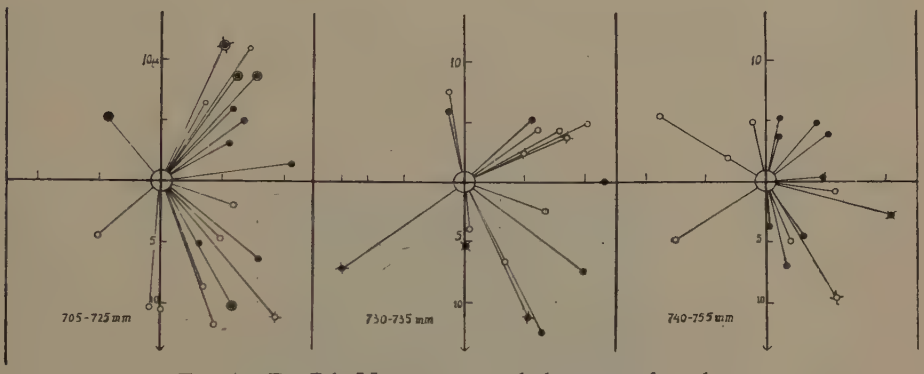

Fig. 4. De Bilt. Microseisms and direction of cyclones.

of each dot to the origin represents the intensity of the microseismic movement. The angle with the vertical is equal to the angle between the direction of the cyclone track and the line connecting its centre with De Bilt.

The diagram for 705—725 mm teaches us another important rule:

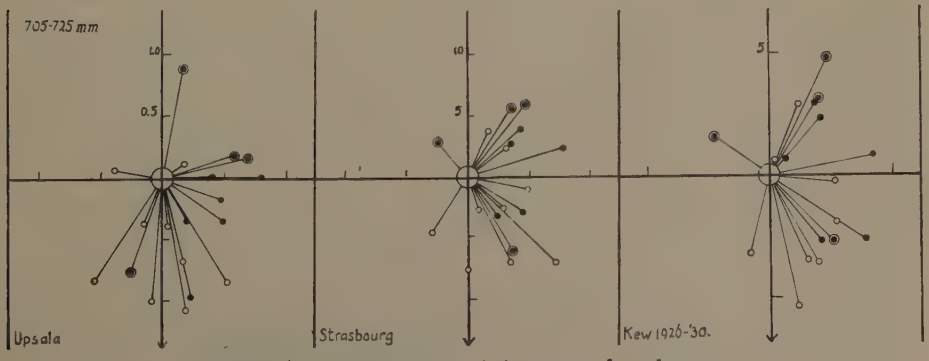

Fig. 5. Microseisms and direction of cyclones.

The microseisms are largest in the direction of the cyclone track.

This same rule is well known for the swell and so we find a close connexion between the two phenomena.

As to less deep depressions the relation is not clearly developed, again because of the obscuring influence of the coast.

When the rule found is real it must hold for other seismographic stations also. Indeed the data of Upsala, Strasbourg and Kew (fig. 5) obviously show the same feature. The long axis of the ellipse-shaped diagram is everywhere directed to the seismograph registering the microseisms.

This concordance needs not wonder us for the stations of De Bilt, Strasbourg and Kew because of their mutual proximity and their similar Galitzin instruments, but it is well supported by the remote station of Upsala, equipped with a 1000 kg Wiechert seismograph.

§ 8. Concerning the aspect of the microseisms GHERZI has stated that the long distance ones are characterized by their occurrence in groups. Indeed this group formation clearly exists in the microseisms of Atlantic origin (fig. 6), but we must remark that this feature is not at all restricted to remote cyclones. These groups are rather common.

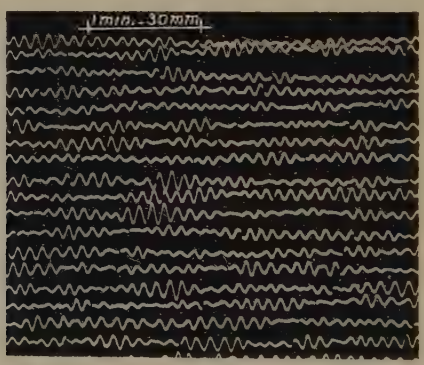

Fig. 6. Microseisms, De Bilt, Dec. 7, 1925.

We recognize the microseisms of coastal or continental origin by their disturbed character with preponderating short and irregular periods. The true long distance microseisms are marked by long regular wave trains and the nice development of groups. The "North sea microseisms" mentioned above have a pure long distance appearance without the small periods of other micros. originating in this same region.

When in the daily weather reports rough sea and nearby depressions or secondaries are wanting, we may be sure that strong and regular microseisms are caused by some remote cyclone. Indeed one of the first features detected by the present research is the frequent occurrence of strong microseisms during ice-days at De Bilt, f.i. December 7, 1925

(fig. 6 and table I). Ice-days in this country point generally to nice calm weather and high pressure. Such "high pressure microseisms" are always due to some Atlantic cyclone at distances up to 3000 km and they may be a "foreshadowing" of changing weather.

§ 9. The microseisms appear to be closely connected with the swell. We may readily presume that the microseisms are caused by the swell.

LEE (l.c.) has mentioned two mathematical objections against this presumption. "The first is that waves in deep water are such that the variation in pressure falls off exponentially with depth so that, when the depth is equal to several wave lengths, the variation of pressure at the bottom is inappreciable. The second objection is that the length of a seawave is very small compared with the length of an elastic wave of the same period in the earth's crust."

"LINKE regards the effective seawaves as those occurring in shallow water quite close to a coastline. In such shallow water the variations of pressure on the sea-bottom are considerable..... There is, however, no satisfactory evidence that microseisms are due to the sea waves in shallow water rather than in deep water."

According to LEE we must not consider an infinite train of regular waves as does the mathematician. The case must be different with actual water waves. There must be disturbances propagated through the water as waves of compression travelling with the velocity of sound and generating, when reaching the bottom, microseismic waves in the ground. LEE remarks that trains of sea waves are equivalent to comparatively small oscillators without fixed phase relation between any two of them. The amounts of energy in the disturbances from different sources can be added. "The grouping of microseismic waves suggests that the phase relations between trains of waves from different sources persist for periods of the order of half a minute. For a little while the displacements due to the several sources cancel out and then the oscillations increase again in amplitude."

Further investigation may elucidate matters. We emphasize the fact that in general the life time of microseisms is much shorter than that of the generating cyclone (cf. table I). Only during a rather short time interval the moving cyclone forces the earth's crust to oscillate. We may point to variations in the slope of the sea-bottom, or perhaps the gradient or the speed of the cyclone, as possible conditions stimulating the process.

I express here my sincere thanks to Prof. VAN EVERDINGEN, whose kind hospitality enabled me to study this matter.

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4) E. GHERZI, Notes de Sismol. Obs. Zi-Ka-Wei, **5**, 1924; **8**, 1926.
5) F. J. W. WHIPPLE, Notes on Mr. A. W. LEE's investigation, Ass. Séism. Publ. Bur. Centr. Intern. Série A, Trav. scient. Fasc. **10**, 1934, p. 127—135. *Note.* LEE's investigation has been published after completion of the present paper; Geoph. Mem. Met. Off. London N°. **62**, 1934.

Physics. — *The compressibility of helium gas between 2.6 and 4.2° K.* By W. H. KEESOM and H. H. KRAAK. Abstract of Communication N°. 234e from the KAMERLINGH ONNES Laboratory at Leiden.

(Communicated at the meeting of November 24, 1934).

Isotherms of helium were determined at the temperatures 4.224, 3.095 and 2.581°K. The results are given in table I.

TABLE I.

Isotherms of helium.				
No.		d_A	$pv_{A\,obs}$	pv_A (obs—calc) $\times 10^6$
4	$T = 4.223^6$ °K	12.619	0.014796	— 2
3	$A_A = 0.015455$	16.716	0.014580	— 1
2		19.963	0.014412	+ 3
1		24.303	0.014174	— 2
5		24.319	0.014176	+ 1
10	$T = 3.094^8$ °K	7.416	0.010957	+ 10
9	$A_A = 0.011325$	9.356	0.010841	— 3
8		10.771	0.010764	— 3
7		12.531	0.010666	— 3
6		24.562	0.009959	+ 1
11	$T = 2.580^6$ °K	8.023	0.009007	
12	$A_A = 0.009443$	11.101	0.008819	

The following values in the formula

$$pv_A = A_A + B_A d_A + C_A d_A^2,$$

or

$$pv_A = A_A(1 + B d_A + C d_A^2)$$

were calculated:

TABLE II.

Virial coefficients of helium.					
T °K	A_A	$B_A \cdot 10^5$	$C_A \cdot 10^7$	$B \cdot 10^3$	$C \cdot 10^6$
4.224	0.015455	—5.151	—0.46	—3.333	— 3.0
3.095	0.011325	—4.880	—2.78	—4.309	—24.5
2.581	0.009443	—4.937	—6.17	—5.228	—65.3

Astronomy. — *Mittlere Lichtkurven von langperiodischen Veränderlichen. XX. R Aquilae.* Von A. A. NIJLAND.

(Communicated at the meeting of November 24, 1934).

Instrumente *S* und *R*. Nahe beim Maximum ist die Schätzung sehr schwierig, da die Vergleichsterne entweder zu hell sind, oder (*A*, *x*) zu weit entfernt. Ich habe beim Maximum 2418543 ohne grossen Erfolg versucht (drei Beobachtungen), durch die Benutzung eines lichtstarken Opernglases diesem Übelstande abzuhelfen. Diese drei Schätzungen sind unberücksichtigt geblieben. Die Beobachtungen wurden alle auf *R* reduziert; die Reduktion *R*—*S* beträgt —0^m.34. Spektrum M5—8e (HA **79**, 184). Gesamtzahl der Beobachtungen 736 (von 2416936 bis 2427709). Es wurden wieder, wie in allen früheren Mitteilungen, die in zwei Instrumenten angestellten Schätzungen nur einmal gezählt. Da eine stark abweichende Schätzung (2418093) verworfen wurde, und der Stern bei der Beobachtung 2425606 unsichtbar war, so bleiben 734 Schätzungen für die Diskussion übrig.

Karte: HAGEN, *Atlas Stell. var. Series III.*

Die Tabelle I gibt eine Übersicht der benutzten Vergleichsterne. Die Sterne *C* und *x* wurden nur ausnahmsweise verwendet. Die photometrischen Helligkeiten stimmen sehr schlecht unter einander: s. z. B. die Sterne *a*, *k* und *m* in HA 74. Zwischen *f* (7^m.6) und *k* (9^m.0) kommt leider in

TABELLE I.

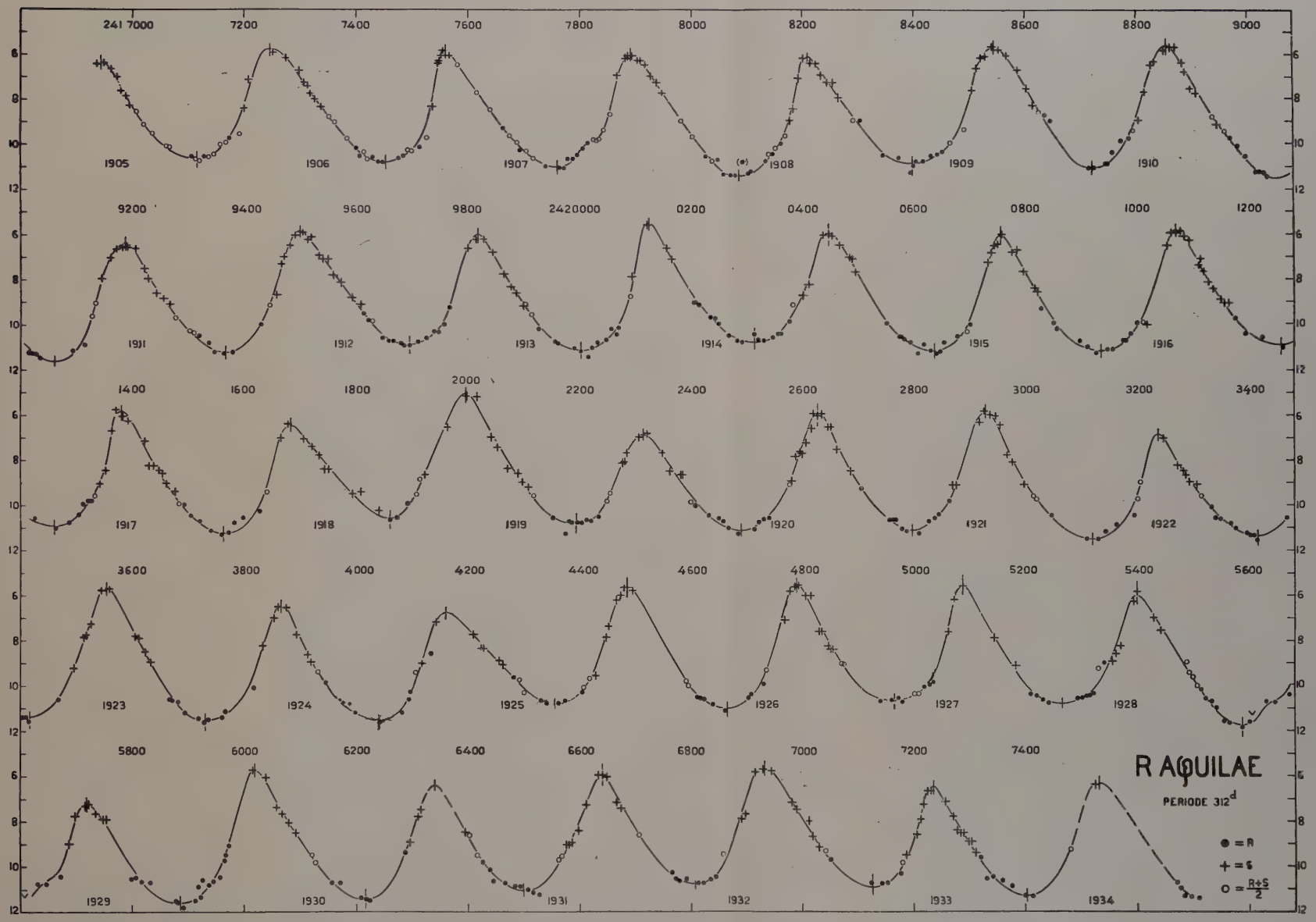
	BD	HAGEN	St.	PD	PD *red*	HA 29	HA 74	HA 97/98	*H*
C	+ 5°.4040	—	65.4	5.42 WG	5.32	5.12	—	5.37 F 2	5.28
A	+ 6.3978	—	62.1	5.60 G—	5.58	—	—	5.66 G 5	5.59
x	+ 6.3989	—	57.7	6.47 GW	6.20	—	6.21	6.38 F 5	6.01
a	+ 8.3951	1	52.8	6.44 G	6.47	6.53	[5.97]	6.62 K 2	6.47
b	+ 5.4081	—	49.8	6.74GW—	6.45	6.46	—	6.34 A 2	6.76
c	+ 6.4014	—	48.0	7.08 WG	7.00	6.90	—	6.88 F 5	6.94
d	+ 6.4021	—	47.4	8.02 GW 7.34 GW	7.73 7.06 6.87	—	—	6.72 F 2	6.99
e	+ 5.4035	—	46.7	7.34 GW	7.06	7.18	—	7.11 A 2	7.06
f	+ 7.3987	—	41.5	7.63 GW	7.35	7.44	—	7.39 A 5	7.55
h	+ 7.3988	—	33.6	—	—	—	—	— G 5	8.29
k	+ 8.3977	5	26.4	—	—	9.00	[8.32]	9.09 B 9	8.97
l	+ 7.3970	7	20.6	—	—	9.16	8.99	—	9.52
m	+ 7.3960	13	16.4	—	—	9.86	[9.43]	—	9.92
μ	+ 7.3952	15	12.3	Grenze	—	—	10.13	—	10.30
n	+ 8.3968	23	6.4	11.08	—	10.97	11.10	—	10.85
p	—	30	0.0	—	—	11.69	11.37	—	11.48

keinem photometrischen Katalog ein passender Vergleichstern vor; insbesondere wäre der photometrische Wert von *h* der genauen Aufstellung der Skala zu statten gekommen.

Stern *n* wurde 14-mal an die Grenze von *S* angeschlossen. Die Stufenskala bezieht sich auf die Helligkeit $8^m.0$; der Stufenwert ist $0^m.095$. Der Anschluss an die photometrischen Helligkeiten ist mit Ausnahme der Sterne *b* und *l* befriedigend.

Es liegen 144 Schätzungen der Farbe vor, welche für fast drei Viertel aus den Jahren 1905 bis 1910 stammen. Aus den Tabellen II*a* und II*b* geht hervor, dass sich die Farbenauffassung im Laufe der Jahre kaum geändert hat; eine Abhängigkeit der Farbe von der Helligkeit ist aber angedeutet: von 6^m bis 10^m vertieft die Farbe sich etwa von $4^c.6$ bis $5^c.5$. Das allgemeine Mittel ist $5^c.01$.

Die Figur 1 enthält die Beobachtungen, alle auf *R* reduziert. Vielleicht müssen die Schätzungen 2424331 — 4404 (5 an der Zahl) um etwa $0^m.7$ niedriger angesetzt werden. Es liegt nämlich die Vermuting nahe, dass hier für die benutzten Vergleichsterne *n* und *p* statt *m* und *n* zu lesen wäre. Auch das Minimum käme dann etwa um $0^m.6$ niedriger zu liegen.


241 7000
7200
7400
7600
7800
8000
8200
8400
8600
8800
9000
1905
1906
1907
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1909
1910
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1918
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1928
5800
6000
6200
6400
6600
6800
7000
7200
7400
1929
1930
1931
1932
1933
1934
R AQUILAE
PERIODE 312d
● = R
+ = S
○ = R+S/2

Fig. 1

TABELLEN IIa und IIb. Farbenschätzungen.

Zeitraum	n	Farbe	Grösse	n	Farbe	Grösse	n	Farbe
		c	m		c	m		c
241 6979—7336	21	5.52	5.78	12	4.67	7.98	12	5.17
7350—7615	21	4.43	5.99	12	5.37	8.64	12	5.33
7638—7907	21	4.71	6.14	12	4.13	9.16	12	5.33
7916—8291	21	5.07	6.34	12	4.52	9.75	12	5.25
8303—8936	20	4.83	6.69	12	4.46	10.11	12	5.08
242 9161—1137	16	5.18	7.18	12	4.96	10.39	12	5.91
2620—7523	24	5.42					144	5.01
	144							

Die Reihe der Abweichungen (Beobachtung minus Kurve) zeigt 242 Plus-, 291 Minuszeichen, 201 Nullwerte, 279 Zeichenfolgen, 253 Zeichenwechsel. Das Mittel der absoluten Werte der Abweichungen ist $0^m.117$.

Ein Einfluss des Mondscheines auf die Helligkeitsschätzung ist nicht bemerkbar. Es verteilen sich auf 291 bei Mondschein angestellte Beobachtungen die Abweichungen wie folgt: 114 Plus-, 109 Minuszeichen, 69 Nullwerte.

Die Tabelle III enthält die aus der Kurve abgelesenen Epochen der Minima m und der Maxima M, nebst einer Vergleichung mit den einfachen Elementen R:

$$2422161^d + 312^d\,E \text{ (für die Minima)}$$

und $$2422288 + 312^d\,E \text{ (für die Maxima).}$$

Aus der Reihe der übrigbleibenden B—R geht hervor, dass in den Jahren 1905—1934 die Periode von R *Aquilae* noch immer in starker Abnahme begriffen war, sogar noch stärker als man es nach den von G. MÜLLER abgeleiteten Elementen (*G u L* II 178), wo ein drittes Glied die Wirkung des quadratischen Gliedes teilweise aufhebt, und auch nach der Neubearbeitung von R. MÜLLER (*Astr. Nachr.* **223**, 186) erwarten würde. Ich möchte mich auch bei diesem Stern wieder zu der Ableitung von Elementen beschränken, welche für die Jahre 1905—1934 die Epochen der Minima und Maxima innerhalb der unvermeidlichen Beobachtungsfehler darzustellen imstande sind. Die durch die Hinzuziehung eines quadratischen Gliedes verbesserten Elemente F lauten:

$$\left.\begin{matrix}2422188^d.4\\2316\ .6\end{matrix}\right\} + 311^d.9\,E - 0^d.278\,E^2,$$

$$\pm 2.63 \qquad 0.18 \qquad 0.020 \text{ (m.F.)};$$

$$\frac{M-m}{P} = 0.411.$$

TABELLE III.

E	Minima m					Maxima M				
	B	v	R	$B-R$	$B-F$	B	v	R	$B-R$	$B-F$
− 17	—	—	—	—	—	241 6944:	m 6.3	6984	− 40	+ 9
− 16	241 7114	m 10.6⁵	7169	− 55	− 12	7246	5.7	7296	− 50	− 10
− 15	7452	10.8	7481	− 29	+ 5	7560	5.8	7608	− 48	− 16
− 14	7760	11.0	7793	− 33	− 7	7890	6.0	7920	− 30	− 6
− 13	8087	11.4	8105	− 18	+ 1	8210	6.1	8232	− 22	− 6
− 12	8400	10.9	8417	− 17	− 5	8545	5.7	8544	+ 1	+ 11
− 11	8721	11.0	8729	− 8	− 2	8853	5.6	8856	− 3	0
− 10	9061	11.6	9041	+ 20	+ 20	9187	6.3	9168	+ 19	+ 17
− 9	9366	11.2	9353	+ 13	+ 7	9500	5.8	9480	+ 20	+ 13
− 8	9695	10.9	9665	+ 30	+ 20	9818	6.0	9792	+ 26	+ 14
− 7	242 0002	11.2	9977	+ 25	+ 11	242 0124	5.5	0104	+ 20	+ 4
− 6	0315	10.8	0289	+ 26	+ 8	0448	5.9	0416	+ 32	+ 12
− 5	0639	11.2	0601	+ 38	+ 17	0757	6.0	0728	+ 29	+ 7
− 4	0937	11.2	0913	+ 24	+ 1	1070	5.8	1040	+ 30	+ 6
− 3	1258	10.9	1225	+ 33	+ 8	1380	5.8	1352	+ 28	+ 2
− 2	1562	11.2	1537	+ 25	− 1	1682	6.4	1664	+ 18	− 10
− 1	1860	10.6	1849	+ 11	− 16	1996	5.0	1976	+ 20	− 8
0	2194	10.8	2161	+ 33	+ 6	2313	6.8	2288	+ 25	− 4
+ 1	2491	11.1	2473	+ 18	− 9	2628	6.0	2600	+ 28	0
+ 2	2799	11.1	2785	+ 14	− 12	2930	5.9	2912	+ 18	− 9
+ 3	3121	11.5	3097	+ 24	− 1	3238	6.8	3224	+ 14	− 12
+ 4	3416	11.4	3409	+ 7	− 15	3554	5.6	3536	+ 18	− 6
+ 5	3730	11.5	3721	+ 9	− 11	3866	6.4	3848	+ 18	− 3
+ 6	4039	11.5	4033	+ 6	− 11	4161	6.7	4160	+ 1	− 17
+ 7	4356	10.8	4345	+ 11	− 2	4485	5.6	4472	+ 13	− 1
+ 8	4665	11.0	4657	+ 8	− 1	4790	5.5	4784	+ 6	− 4
+ 9	4966	10.7	4969	− 3	− 7	5089	5.5	5096	− 7	− 12
+ 10	5266	10.8	5281	− 15	− 13	5400	6.0	5408	− 8	− 8
+ 11	5588	11.7	5593	− 5	+ 3	5718	7.2	5720	− 2	+ 4
+ 12	5886	11.6	5905	− 19	− 5	6020	5.7	6032	− 12	+ 1
+ 13	6216	11.5	6217	− 1	+ 20	6340:	6.4	6344	− 4	+ 16
+ 14	6499	11.1	6529	− 30	− 1	6640	6.0	6656	− 16	+ 11
+ 15	6806	10.7	6841	− 35	+ 3	6932	5.6	6968	− 36	0
+ 16	7126	10.9	7153	− 27	+ 19	7236	6.4⁵	7280	− 44	0
+ 17	7403	11.3	7465	− 62	− 7	7532:	6.3	7592	− 60	− 8
		11.10			± 8		6.00			± 8

Aus den mitgeteilten mittleren Fehlern, sowie aus der Tatsache, dass in der Spalte der *B—F*, sowohl bei den Minima wie bei den Maxima, die Zeichenfolgen stark überwiegen, geht hervor, dass das Resultat keineswegs befriedigend zu nennen ist. Es hat aber keinen Zweck, durch weitere Rechnungen einen besseren Anschluss zu erzielen; das muss späteren Untersuchungen überlassen bleiben.

PRAGER's Katalog für 1934 gibt den Periodenwert $305^d.4$ und das aus sämtlichen von mir seit d. J. 1905 in den *Astr. Nachr.* mitgeteilten Epochen der Minima und Maxima abgeleitete allgemeine Mittel ist 312^d.

Die extremen Werte des Lichtwechsels sind:

$$\left.\begin{array}{l} \text{Minimum: } v = 11^m.10 \pm 0^m.098 \\ \text{Maximum: } v = \ 6 \ .00 \pm 0 \ .142 \end{array}\right\} \text{(m.F.)}.$$

Die Amplitude beträgt somit $5^m.10$. Sowohl beim Minimum wie beim Maximum scheinen die Abweichungen vom Mittelwert regellos aufzutreten. Jedenfalls ist von einer allmähligen Vergrösserung der Amplitude — sei es durch Erhöhung der Maxima, oder durch Erniedrigung der Minima — welche die *G und L*, übrigens mit grossem Vorbehalt, erwähnt, nichts zu bemerken.

Es wurde wieder der mittlere Verlauf der Lichtkurve in der Umgebung der beiden Hauptphasen durch Ablesung der Helligkeit für je 10^d abgelesen. Bei den Maxima 2417890, 2425400 und 5918 sind Verzögerungen im Aufstieg angedeutet; sonst verläuft der Lichtwechsel glatt, und in meinen Beobachtungen ist von Nebenmaxima, Stillständen oder kleinen Erhebungen auf dem absteigenden Lichtzweige (*G und L*) nichts zu bemerken.

Die beiden Teilkurven schliessen sich genau an einander an (s. die

TABELLE IV. Die mittlere Kurve.

Phase	v	Phase	v	Phase	v	Phase	v	Phase	v
d	m	d	m	d	m	d	m	d	m
— 100	9.06	— 30	10.90	+ 40	10.63	+ 110	6.64	+ 180	7.84
— 90	9.41	— 20	11.01	+ 50	10.35	+ 120	6.08	+ 190	8.25
— 80	9.76	— 10	11.08	+ 60	10.02	+ 130	6.03	+ 200	8.65
— 70	10.06	— 0	11.10	+ 70	9.54	+ 140	6.22	+ 210	9.00
— 60	10.33	+ 10	11.09	+ 80	8.91	+ 150	6.61	+ 220	9.35
— 50	10.55	+ 20	11.01	+ 90	8.19	+ 160	7.02		
— 40	10.73	+ 30	10.85	+ 100	7.40	+ 170	7.43		

Fig. 2) und geben zusammen den Verlauf der mittleren Kurve (Tabelle IV).

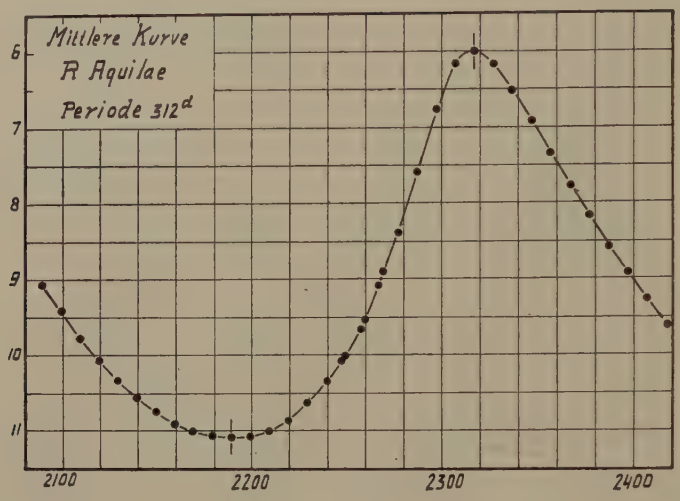

Fig. 2

Die Streuung in der Nähe von 50^d erreicht die Werte:

	m	M	Mittel
im aufsteigenden Aste:	$0^m.128$	$0^m.376$	$0^m.252$
im absteigenden Aste:	0 .098	0 .250	0 .174
Mittel:	0 .113	0 .313	

Die Streuung ist wieder grösser beim Maximum und grösser im aufsteigenden Aste. Das Verhältnis der Streuungen $0^m.252$ und $0^m.174$ ist 1.45, das Verhältnis der durchschnittlichen Geschwindigkeiten des Lichtwechsels bei Auf- und Abstieg 1.43.

Utrecht, November 1934.

Chemistry. — *Complex Salts of α-α'-Dipyridyl with Zinc and Cadmium.* By F. M. JAEGER and J. A. VAN DIJK.

(Communicated at the meeting of November 24, 1934).

§ 1. In a series of papers from this laboratory [1]) we already described a number of complex salts of bivalent *iron, nickel* and *copper* with *α-α'-dipyridyl*. In the present paper the results are communicated of an analogous investigation concerning the complex ions of the same base with *zinc* and *cadmium*.

§ 2. *Zinc salts.* If to a solution of *zinc sulphate*: $ZnSO_4 + 7H_2O$ *three* equivalents of dipyridyl are added, colourless crystals are deposited on slow evaporation in vacuo at room-temperature, which, on analysis, prove to be *tridipyridyl-zinc sulphate* + $7\ H_2O$; found: 8,53 % *Zn*, 11,13 % *N*, and 16,66 % H_2O; calculated: 8,64 % *Zn*, 11,12 % *N*, and 16,69 % H_2O.

The monoclinic crystals are completely isomorphous with the corresponding *nickel-* and *copper salts*.

Monoclinic-prismatic.

$$a : b : c = 1{,}5389 : 1 : 0{,}9132;$$
$$\beta = 82° 13\tfrac{1}{2}'.$$

Forms observed: $a = \{100\}$, $r = \{101\}$, and $s = \{\bar{1}01\}$, almost equally broad, $\{100\}$ mostly being somewhat better developed than the others;

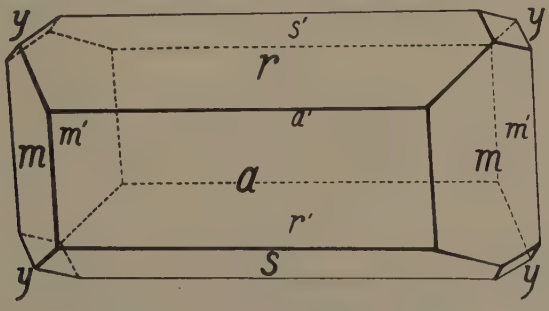

Fig. 1. Crystalform of Tridipyridyl-Zinc sulphate $(+7\ H_2O)$.

$m = \{110\}$, rather broad and lustrous; $y = \{011\}$, small, but well measurable. The crystals are thick-prismatic and somewhat elongated parallel to the *b*-axis. (Fig. 1).

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[1]) F. M. JAEGER and J. A. VAN DIJK, Proceed. R. Acad. of Sciences, Amsterdam, **37**, (1934), 10, 333, 395. In the course of these investigations attention was drawn to the remarkable fact that the special type of the possibly occurring complex ions often proves to be dependent on the specific nature of the anion of the salts used in these experiments.

Angular Values:	*Observed:*	*Calculated:*
$a:r = (100):(101) =$*	53° 40′	—
$a:s = (\bar{1}00):(\bar{1}01) =$*	65 11	—
$a:m = (100):(110) =$*	56 44½	—
$r:s = (101):(\bar{1}01) =$	61 9	61° 9′
$m:m = (110):(\bar{1}10) =$	66 31	66 31
$m:y = (1\bar{1}0):(011) =$	51 57	51 58⅓
$y:s = (011):(\bar{1}01) =$	51 14	51 20
$m:s = (1\bar{1}0):(10\bar{1}) =$	76 49	76 41½
$m:r = (110):(101) =$	71 3	71 2
$y:r = (011):(10\bar{1}) =$	49 17	49 22
$m:y = (110):(011) =$	59 34	59 36

No distinct cleavability was observed.

From a solution of the original zinc sulphate with *two* equivalents of dipyridyl first a white, only slightly soluble salt, crystallizing in small needles, is deposited; subsequently thick crystals of the tridipyridyl salt just mentioned can be obtained from the mother-liquor. The white, less soluble salt proves to be a *mono*dipyridyl salt of the composition; $\left\{ Zn \begin{matrix} (Dipyr) \\ (H_2O)_2 \end{matrix} \right\} (SO_4)$. Analysis yielded: 18,34 % Zn; 7,92 % N; 28,28 % (SO_4); 9,41 % H_2O; theoretically: 18,49 % Zn; 7,92 % N; 27,17 % (SO_4), and 10.19 % H_2O. The water is not driven out in a vacuum above sulphuric acid, but only after heating at 150° C., so that, with respect to the co-ordination number *four*, it is most probable that the 2 molecules of water form part of the complex. The percentage of the (SO_4) is always a little too high, — which seems to indicate that part of the water can be substituted by (SO_4), exactly as was observed in the case of the corresponding *iron* salt. Also from the solution of the zinc sulphate with *one* equivalent of dipyridyl this *mono*dipyridyl salt is deposited. A *di*dipyridyl salt seems not to be formed in aqueous solutions.

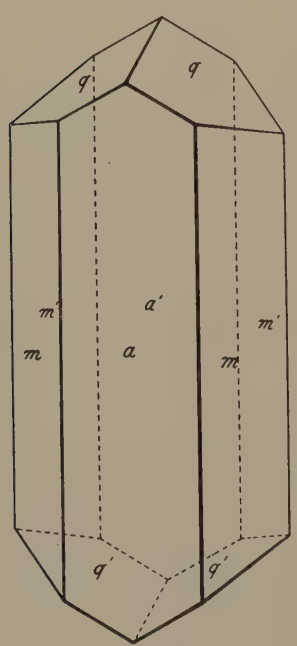


Fig. 2. Crystalform of Monodipyridyldiaquo-Zinc sulphate.

Monodipyridyl-diaquo-zinc sulphate crystallizes from its aqueous solutions in very small, thin monoclinic needles.

Monoclinic-prismatic.

$a:b:c = 1{,}217:1:0{,}531$;

$\beta = 77° 5'$.

Forms observed: $a = \{100\}$, broader than $m = \{110\}$; $q = \{011\}$, all

yielding sufficiently sharp reflections. The crystals are prismatic, with their elongation in the direction of the *c*-axis.

Angular Values:[1])	*Observed:*	*Calculated:*
$a:m = (100):(110) =^*$	49° 52′	—
$m:q = (110):(01\bar{1}) =^*$	61 22	—
$m:q = (\bar{1}10):(011) =^*$	77 6	—
$q:q = (011):(0\bar{1}1) =$	54 44	54° 42′
$a:q = (100):(011) =$	78 28	78 33
$m:m = (110):(\bar{1}10) =$	80 16	80 16

A distinct cleavability could not be stated.

On {100} an axial image may be occasionally observed; the plane of the optical axes is {010}, the first bissectrix being almost perpendicular to {100}. Strong, inclined dispersion.

§ 3. The same experiments now were made, *zinc chloride* being used instead of the sulphate.

From the solution of 1 mol. (*zinc chloride* + $1\frac{1}{2}H_2O$) + 1 mol. *dipyridyl* a colourless salt crystallizes in the shape of intergrown, irregularly bordered needles; its solubility is about the same as, or at least comparable with, that of the *tri*dipyridyl salt to be described later on.

Analysis yielded: 22,31 % *Zn* (in the anhydrous salt); 9,41 % *N*; no loss of water, even at 150° C., occurred; for the *monodipyridyl-zinc-chloride*: $\left\{ Zn \begin{matrix} (Dipyr) \\ Cl_2 \end{matrix} \right\}$ is calculated: 22,36 % *Zn* (in the anhydrous salt); 9,58 % *N*.

The salt is more soluble than the corresponding *cupric* salt formerly described. It may be that also a *mono*dipyridyl salt with two molecules of water can exist.

§ 4. From a solution of zinc chloride to which 2 or 3 equivalents of dipyridyl are added, flat colourless crystals of the *tridipyridyl-zinc-chloride* are deposited. They crystallize with 7 molecules of water, as may be seen from the following data:

On analysis they yielded: 9,05 % *Zn*, 11,30 % *N*, and 17,47 % H_2O; theoretically: 8,95 % *Zn*; 11,50 % *N*, and 17,25 % H_2O.

Tridipyridyl-Zinc-Chloride: $\{Zn\ (Dipyr)_3\}\ Cl_2 + 7\ H_2O$, crystallizes from its aqueous solutions in small, strongly refracting, colourless crystals or parallelogram-shaped, thin plates.

Monoclinic-prismatic.

$a:b:c = 0{,}6304:1:2{,}1051$;

$\beta = 72° 43'$.

Forms observed: $c = \{001\}$, predominant and very lustrous; $m = \{110\}$,

[1]) These values were measured by means of the bicircular goniometer by Mr. W. J. VAN WEERDEN, candidate of chemistry, at this laboratory.

yielding very sharp reflections; $q = \{011\}$, small, but very well measurable; $a = \{100\}$, very narrow, yielding feeble reflections; sometimes very

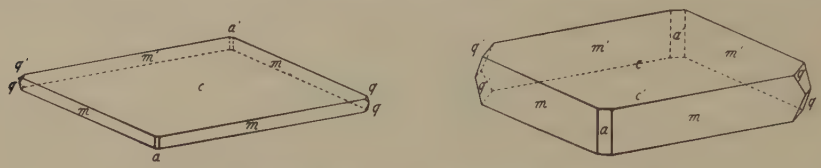


Fig. 3. Crystalforms of Tridipyridyl-zinc-chloride.

narrow, $\omega = \{118\}$ and $\varepsilon = \{115\}$, dull and only approximately measurable. The crystals are flattened parallel to {001}.

Angular Values:	*Observed*:	*Calculated*:
$c : m = (001) : (110) =$	$75^\circ\ 5'$	—
$c : q = (001) : (011) =$	$63\ 33$	—
$m : m = (110) : (1\bar{1}0) =$	$59\ 54$	—
$m : q = (110) : (011) =$	$55\ 24$	$55^\circ\ 39'$
$m : a = (110) : (100) =$	$29\ 57$	$29\ 57$
$a : c = (100) : (001) =$	$72\ 53$	$72\ 43$
$c : \omega = (001) : (118) =$	$22\ 45$	$22\ 30$
$c : \varepsilon = (001) : (115) =$	ca. 33°	$31\ 53$

No distinct cleavability was observed.

The plane of the optical axes is perpendicular to {010} and practically perpendicular to {001}, so that the normal on {001} is the first bissectrix, probably of positive character, although the birefringence is so weak that no accurate determination is possible. The apparent axial angle is rather small, about of medium size; the dispersion is strong: $\varrho < v$ and has an apparently rhombic character.

Evidently only the *mono-* and *tri*dipyridyl salts are formed in the case of zinc *chloride*, — exactly as in the case of the corresponding *sulphate*.

§ 5. *Cadmium salts.* Solutions of *cadmium nitrate* were mixed with 1, 2 or 3 equivalents respectively of dipyridyl and slowly evaporated at room-temperature. The solution containing 3 molecules of dipyridyl yielded long, slightly soluble, colourless needles, which, on analysis, proved to correspond to a *di*-dipyridyl salt of the composition: $\{Cd\,(Dipyr)_2\}\,(NO_3)_2 + \frac{1}{2}\,H_2O$; found: 20,15 % *Cd*, 14,98 % *N* and 1,62 % H_2O; calculated: 20,16 % *Cd*, 15,07 % *N*, and 1,62 % H_2O.

From the mother-liquor the corresponding *tri-dipyridyl-cadmiumnitrate*: $\{Cd\,(Dipyr)_3\}\,(NO_3)_2 + 7\,H_2O$ crystallizes, as was proved by analysis: 13,67 % *Cd*, 13,64 % *N*, 15,12 % H_2O; theoretically: 13,53 % *Cd*, 13,47 % *N*, and 15,18 % H_2O. The crystals soon lose their water of crystallization when exposed to the air.

Also from a solution of the nitrate with 2 equivalents of dipyridyl, the *di*-dipyridyl salt just mentioned is primarily deposited; however, from the mother-liquor later on colourless rhombic crystals are deposited, which

have *the same* composition and which — as far as the very badly developed needles first mentioned allowed a measurement by means of the bicircular goniometer — seem to have also the same crystallographical form as the needles of the *di*dipyridyl salt mentioned above.

Finally from a solution of cadmium nitrate + 1 equivalent of dipyridyl colourless, lustrous crystals are formed, which proved to be $\left\{ Cd \begin{matrix} (Dipyr) \\ (H_2O)_2 \end{matrix} \right\} (NO_3)_2$; they already lose their water in vacuo at room-temperature. The crystals commonly are badly developed and often show curved faces. On analysis they proved to contain: 26,40 % *Cd*; 13,03 % *N*, and 8,10 % H_2O; theoretically: 26,23 % *Cd*, 13,07 % *N*, and 8,40 % H_2O.

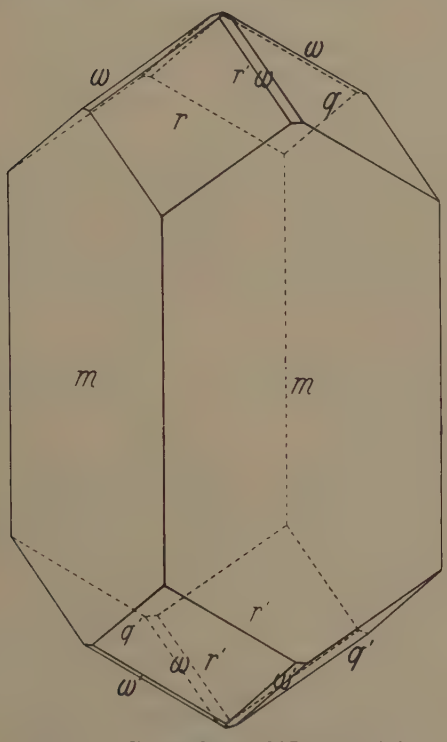


Fig. 4. Crystalform of Tridipyridyl-cadmium nitrate.

§ 6. *Tridipyridyl-Cadmiumnitrate:* $\{Cd\ (Dipyr)_3\}\ (NO_3)_2 + 7H_2O$ crystallizes in small, rather isometrically developed crystals, which soon become opaque, so that rapid measurements have to be made. The crystals are badly built: in the zone $m:r:q:m$ the angular values are appreciably oscillating, the differences for the same angles amounting from 1° to 4°, and in the zone $m:m$ from 1° to 2°.

Rhombic-bipyramidal.
$a:b:c = 0{,}9011:1:0{,}8232.$

The forms observed are: $m = \{110\}$, broad, well reflecting; $r = \{101\}$ and $q = \{011\}$, about equally large, often yielding dull reflections; $\omega = \{112\}$, very small, sometimes absent. The habitus of the crystals is thick-prismatic, occasionally elongated parallel to the *c*-axis.

Angular Values:	*Observed:*	*Calculated:*
$m:m = (110):(1\bar{1}0) =^*$	84° 3′ (83° 30′—84° 30′)	—
$m:r = (110):(101) =^*$	59 56 (59°—61°)	—
$r:q = (101):(011) =$	55 48 (53° 30′—57° 30′)	55° 15′
$q:m = (011):(\bar{1}10) =$	64 16 (63° 40′—65° 30′)	64 49
$r:\omega = (101):(112) =$	27 18 (26° 30′—28° 30′)	26 46½
$\omega:q = (112):(011) =$	28 30 (28° -29° 30′)	28 28½

No distinct cleavability was observed.

Here the remarkable fact can be stated that in its habitus as well as in its angular values, this salt shows a complete analogy, not discernible from real isomorphism, with: $\{Fe\,(Dipyr)_3\}\,Cl_3 + 7\,H_2O$; i.e. an isomorphism appears to exist here between a *nitrate* and a *chloride* of the same type.

Solutions of both salts were mixed in very different proportions and left to crystallize at room-temperature. In all cases only red, completely homogeneous mixed crystals were deposited, so that the perfect miscibility of the two compounds in the solid state is proved beyond all doubt.

§ 7. *Didipyridyl-Cadmiumnitrate*: $\{Cd\,(Dipyr)_2\}\,(NO_3)_2 + \frac{1}{2}H_2O$ is rhombic. On slow evaporation of the solution at room-temperature the salt crystallizes in big, flat colourless plates, with hexagonal boundaries.

They are rhombic-bipyramidal, with:

$$a : b : c = 1{,}2283 : 1 : 1{,}2034.$$

Forms observed: $o = \{122\}$, very lustrous and well developed as terminal faces of the elongated tables; $a = \{100\}$, predominant, vertically striated and yielding bad and multiple reflections; $m = \{110\}$, narrow, mostly dull and often striated; $b = \{010\}$, narrow, but very lustrous.

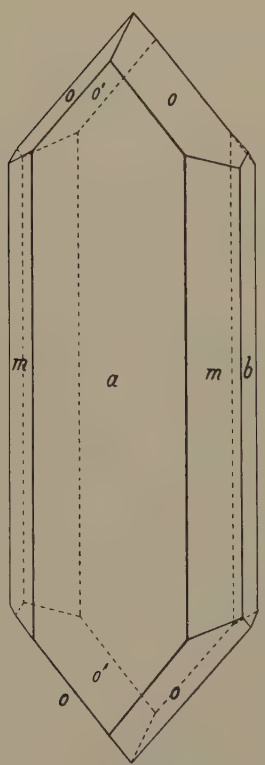


Fig. 5. Crystalform of Didipyridyl-Cadmium nitrate.

Angular Values:	*Observed*:	*Calculated*:
$o : o = (122) : (1\bar{2}2) =$	94° 27′	—
$o : o = (122) : (\bar{1}22) =$	34 46	—
$o : b = (122) : (010) =$	42 45	42° 46½′
$a : o = (100) : (122) =$	72 37	72 37
$a : m = (100) : (110) =$	50 38	50 51
$m : b = (110) : (010) =$	39 22	39 9

No distinct cleavability was found; perhaps one parallel to *b* is present.

On the faces of the vertical zone the optical extinction is perpendicular to the *c*-axis. The plane of the optical axes is {001}, with *a* as the first, positive bissectrix. The apparent axial angle is rather small; strong dispersion.

The fine needles first separated out from the solutions of cadmium nitrate and 2 equivalents of dipyridyl were measured by Dr. TERPSTRA by means of the bicircular goniometer. The crystals are so small and so badly developed that it appeared hardly possible to decide whether they are monoclinic or rhombic: in the latter case their axial ratio must approximately be: $a : b : c = 2{,}6 : 1 : 1{,}28$, with the forms: {100} and {111}

and with {001} as the plane of the optical axes, the *a*-axis being the first, positive bissectrix. If we take into account that the pyramid of the thicker crystals described above really is {122}, so that the approximate axial ratio of the needles then would become: $a : b : c = 1{,}3 : 1 : 1{,}28$, that moreover, the optical properties of the latter are completely analogous to those of the big crystals, and that the chemical composition also is the same, — then it seems allowable to conclude from this evidence that the two preparations are *identical*.

§ 8. The *Mono-dipyridyl-Cadmium nitrate*: $\left\{ Cd \begin{matrix} (Dipyr) \\ (H_2O)_2 \end{matrix} \right\} (NO_3)_2$ crystallizes in aggregates of thin, rectangularly shaped plates of monoclinic symmetry; the individual crystals are very lustrous and yield sharp reflections, but gradually they become opaque.

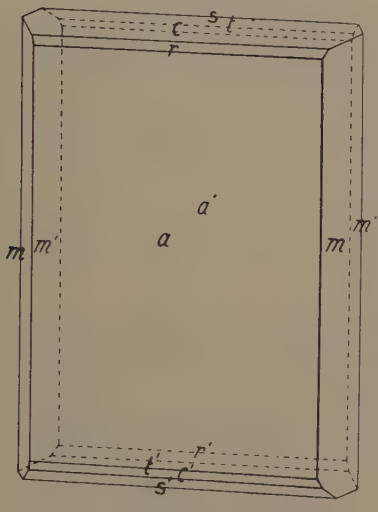


Fig. 6.

Monoclinic-prismatic.
$a : b : c = 2{,}5505 : 1 : 1{,}6981$;
$\beta = 74° 14'$.

Forms observed: $a = \{100\}$, predominant and very lustrous; $m = \{110\}$ and $c = \{001\}$, about equally broad and yielding very sharp reflections; $r = \{101\}$, somewhat narrower than $s = \{\bar{1}01\}$, both very well reflecting; $t = \{\bar{3}05\}$, often absent, sometimes only present with *a*, *m*, and *c*. The habitus of the crystals is tabular parallel {100}, with a slight elongation in the direction of the *c*-axis. (Fig. 6).

Angular Values:	*Observed*:	*Calculated*:
$a : m = (100) : (110) =$*	67° 50′	—
$a : r = (100) : (101) =$*	45 45	—
$r : c = (101) : (001) =$*	28 29	—
$m : m = (110) : (\bar{1}10) =$	44 20	44° 20′
$c : s = (001) : (\bar{1}01) =$	37 52	38 2
$s : a = (\bar{1}01) : (\bar{1}00) =$	67 54	67 44
$c : t = (001) : (\bar{3}05) =$	56 52	56 $48\frac{3}{4}$
$c : m = (001) : (110) =$	84 7	84 7
$m : r = (110) : (101) =$	74 48	74 44
$m : s = (\bar{1}10) : (\bar{1}01) =$	81 45	81 $46\frac{1}{2}$

No distinct cleavability was observed.

On {100} normal extinction, on {110} under a small angle with the direction of the *c*-axis.

In the near future we hope to be able to communicate the results obtained with some other *cadmium* salts of this type.

Groningen, Laboratory for Inorganic and Physical Chemistry of the University.

Chemistry. — *Isomerism of the cyclic isoprene sulphones.* By J. BÖESEKEN and E. DE ROY VAN ZUYDEWIJN.

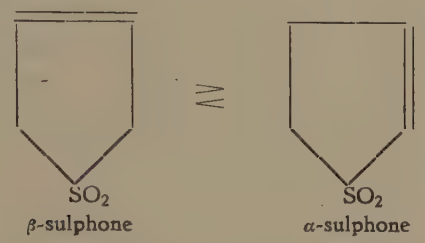
(Communicated at the meeting of November 24, 1934).

On the ground of theoretical considerations INGOLD and ROTHSTEIN (Journ. Chem. Soc. **1929**, 8) concluded that strongly positive groups, such as $-\overset{+}{N}R_3$ and $-\overset{+}{S}O_2R$, in the presence of KOH, are able to activate a potentially mobile three-carbonsystem, to which they are attached. They demonstrated it for the first group; in unsaturated sulphones of the type R-SO_2-propenyl this did not succeed, owing to linkage of H-OH to the double bond (Journ. Chem. Soc. **1934**, 684).

It is to be expected, therefore, that the transposition of the cyclic isoprene-sulphone in alkaline solution under the influence of ultraviolet light, found by EIGENBERGER (Journ. prakt. Chem. [2], **129**, 312 (1931)), of which we already pointed out the improbability of a cis-trans conversion (Rec. trav. chim. **53**, 673 (1934)), is a tautomeric transposition. In that case not the application of ultraviolet rays, but KOH would be essential to the transposition; indeed also after ten days *in the dark* the cyclic isoprene sulphone dissolved in 0.5 n KOH is for a considerable part converted into its isomer. The light only has an accelerating effect. Whereas in isoprene sulphone the equilibrium appears to be situated far to the side of the isomer, we found as the result of some preliminary observations that this is not the case in the cyclic sulphone of butadiene. Either by exposure to light or by simply leaving a solution in 0.5 n KOH for some days, from the butadiene sulphone melting at 63°, regularly an oil is formed which does not set even in ice and salt.

The decomposition at 180° of the ordinary butadiene sulphone was made use of in order to separate it from the formed stabler isomer. A substance was left behind which is a solid at the usual temperature (meltingpoint 45—50°) and could be distilled without decomposition in the cathode-vacuum (yield about $^1/_3$ of the original sulphone). On rubbing together this isomer with the original substance, we again obtained a non-setting oil.

Being exposed to the action of 0.5 n KOH, the isomer changes again into an oil, which dit not solidify at 0°. Very likely we have to deal here with an equilibrium:



β-sulphone α-sulphone

which is apparently situated at about $^2/_3$ β and $^1/_3$ α.

The constitution of the isomeric cyclic isoprene sulphone was proved by us by means of ozonization, according to the method previously described [1]), in a mixture of equal volumes of chloroform and water.

The ozonization product was freed from HCl and formic acid in a vacuum essicator above KOH, and the residue neutralized with $BaCO_3$.

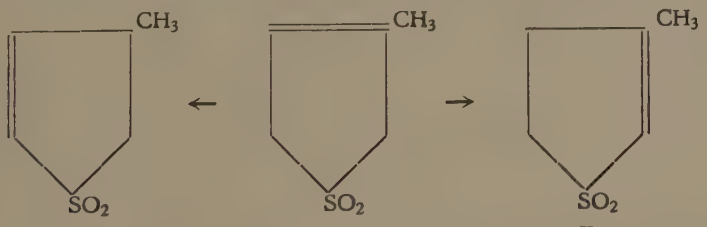
The Barium salt, recrystallized from water and alcohol, produced the following figures of analysis.

C = 22.1 and 21.5 %. H = 3.6 and 3.6 %. S = 14.6 %.
Ba = 31.1 and 30.9 %.

Calculated for: $Ba_{\frac{1}{2}}O_3SCH_2CH_2COCH_3$ or $Ba_{\frac{1}{2}}O_3SCH_2CH(CH_3)\text{-}CHO$

C = 21.8 %. H = 3.2 %. S = 14.5 %. Ba = 31.1 %.

This Barium salt had very slightly reducing properties. With an alkaline solution of Bromine, however, it produced bromoform. Consequently there are indications for an aldehydic acid as well as for a ketonic acid. Here also the double bond is shifted from the β- to the α-position.



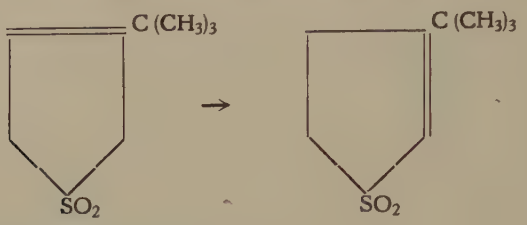
I II

This may give rise to two isomers; in view of the potassium (and light) stability of the dimethyl-butadiene sulphone we chiefly expected isomer I. This appears to be not the case. A quantitative determination will have to explain this, when it has also to be considered whether indeed equilibria are established between the three isomers. At any rate this investigation has done away with the exceedingly improbable representation of EIGENBERGER [2]), assuming the isomerwation to be a cis-trans-conversion.

[1]) Recueil **53**, 673 (1934).

[2]) J. Prakt. Ch. [2] **127**, 307 (1930); **129**, 312; **131**, 289 (1931).

Finally we remark that from the dissertation recently published by J. STRATING, Groningen, it appears that, in the investigation of the cyclic tertiary butyl-butadiene sulphone and its isomer by means of the same ozonization method, he arrived independently at the same result. The isomer isolated by him had, as appeared from the oxidation products,



the structure represented above.

Delft, 24th November 1934.

Embryology. — *Über die Determination der fötalen Augenspalte bei Amphibien.* Von M. W. WOERDEMAN.

(Communicated at the meeting of November 24, 1934).

Über das im Titel angegebene Problem liegt eine Untersuchung vor von SATO (1933), der schon auf der Versammlung der Deutschen Zoologischen Gesellschaft in Utrecht (1931) über seine vorläufigen Resultate einen Vortrag hielt. Bei der Diskussion habe ich damals mitgeteilt, dass ich zur Beantwortung einer anderen Frage mit ähnlichen Experimenten beschäftigt war und in manchen Hinsichten zu demselben Resultate gekommen war. An anderer Stelle habe ich über diese Untersuchungen berichtet (Zeitschr. f. mikr. anat. Forschung, Bnd. 36, 600, 1934. Festschrift für BOEKE).

Hier werde ich nun einige Wahrnehmungen beschreiben, welche als Ergänzung der Arbeit von SATO betrachtet werden können.

Der genannte Autor hat bei Keimen von Triton taeniatus (Neurulae mit eben geschlossenem Neuralrohr und gestreckte Embryonen mit träger Bewegung und erstem Pigment) die Augenanlage umstochen, samt der darüber liegenden Epidermis herausgeschnitten, um 180° um ihre proximo-distale Achse gedreht, wieder eingepflanzt und zur Einheilung gebracht.

Es treten dann nachher Larven auf mit einer herkunftsgemäss entwickelten dorsalen, oder mit ortsgemässer ventraler Augenspalte, und Larven mit abweichender Richtung der Spalte oder mit zwei, event. drei Spalten. Offenbar sind die Einstülpungs- und Wachstumstendenzen, welche zur Ausbildung der Spalte notwendig sind, bei den Versuchstieren, welche eine herkunftsgemässe Augenspalte entwickelten, schon determiniert

gewesen. Wenn sich aber eine ortsgemässe ventrale Spalte entwickelt, oder wenn das Auge nachher eine dorsale und eine ventrale Spalte besitzt, so muss man annehmen, dass diese Wachstumstendenzen und die Einstülpungsstelle nicht endgültig determiniert waren und Umgebungsfaktoren bei der endgültigen Determination der Spalte mitgewirkt haben.

SATO kommt also zu der Schlussfolgerung, dass die Richtung der fötalen Augenspalte durch zwei Faktorengruppen bestimmt wird, nämlich: durch dem Auge inhärente Einstülpungs- und Wachstumsvorgänge und durch Umgebungsfaktoren (nachträgliche ventrale Verbindung mit dem Gehirn.).

Die Verteilung der einzelnen Versuchsergebnisse auf die Operationsstadien sei nach dem Autor zu erklären durch die Annahme, dass die Determination der inhärenten Wachstumsvorgänge im Laufe der Operationsperiode erfolgte und nachher immer stabiler wurde.

Nun besteht noch immer Ungewissheit über die Frage, in welchem Grade die zukünftige Augenstruktur schon in der Neuralplatte determiniert sei.

Da ich nicht nur Experimente ausgeführt habe, die denjenigen von SATO ähnlich sind, sondern auch jüngere Operationsstadien (Keime mit eben angedeuteter Neuralplatte) benutzt habe, können meine Versuche die Ergebnisse SATO's für jüngere Entwicklungsstadien ergänzen und zu gleicher Zeit einen Beitrag liefern zur Beantwortung der Frage nach dem Determinationszustand der Augenanlage in der Neuralplatte.

Meine Versuchstiere waren Keime von Triton taeniatus, Rana esculenta und Axolotl. An der rechten Seite wurde das augenbildende Bezirk der eben sichtbaren Neuralplatte [Augenplatte, MANCHOT (1929) und WOERDEMAN 1929)] umschnitten, von der Unterlage freipräpariert und dann (also ohne Unterlagerung) um 90° gedreht und wieder eingepflanzt.

Die Verklebung der Neuralwülste im Operationsgebiet war manchmal etwas verzögert, oft nicht ganz normal. Es bildeten sich in sehr vielen Fällen abnormale Augen. Doch auch fand ich bei meinen Versuchstieren Augen, die normal entwickelt waren.

Bei den abnormalen Augen wurde die Richtung der fötalen Augenspalte genau untersucht und es stellte sich nun dabei heraus, dass:

a. Augen gebildet waren mit schiefstehender Augenspalte,
b. mit geknickter Spalte, und
c. mit einer herkunftsgemässen und einer ortsgemässen Spalte.

Von jeder der drei Richtungsabweichungen gebe ich ein Beispiel. In Abb. 1 *A* ist eine Neurula von Rana esculenta abgebildet, bei der einige Stunden zuvor die rechte Augenplatte ohne Unterlagerung um 90° gedreht war. Der mediale Teil der Augenplatte ist jetzt nach hinten gedreht.

In Abb. 1 *B* sieht man ein Wachsplattenmodell des Auges, welches sich aus der gedrehten Anlage entwickelt hat. Die fötale Augenspalte ist noch weit offen und steht schief (Pfeil 3), wie man aus der Richtung des Augenstiels (Pfeil 1) sehen kann. Wäre die Spalte herkunftsgemäss

entwickelt, so hätte sie in der Richtung des Pfeiles 2 stehen müssen. Eine geringe Abweichung der Richtung weist darauf hin, dass sie sich auch nicht vollkommen ortsgemäss (Pfeil 1) entwickelt hat.

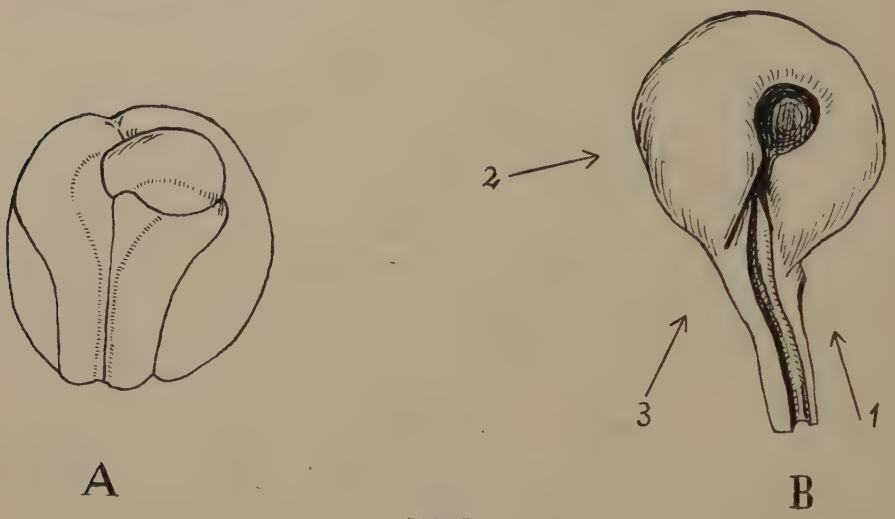


Abb. 1.

Bei einem anderen Keim von Rana esculenta, bei dem dieselbe Operation ausgeführt war, wie die in Abb. 1 *A* abgebildete, entwickelte sich das Auge der Abb. 2.

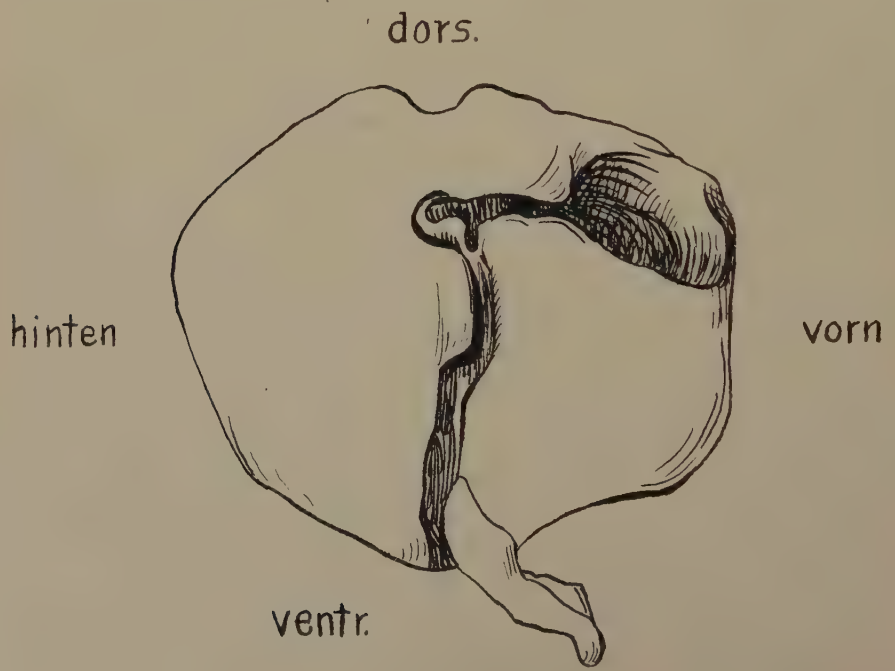


Abb. 2.

Es ist wiederum ein rechtes Auge. Die fötale Augenspalte ist zuerst nach hinten gerichtet, biegt dann aber rechtwinklig nach der ventralen Seite um, und setzt sich auf den Augenstiel fort.

Der nach hinten gerichtete Abschnitt der Spalte hat sich herkunftsgemäss entwickelt. Der nach ventral umgebogene Abschnitt entspricht der ortsgemässen Richtung.

Abb. 3 *A* zeigt einen Tritonkeim, sofort nach der Operation, wobei die rechte Augenplatte derart gedreht wurde, dass ihr medialer Rand nach vorn gekehrt wurde. Der Keim entwickelte sich langsam, nach 12 Stunden

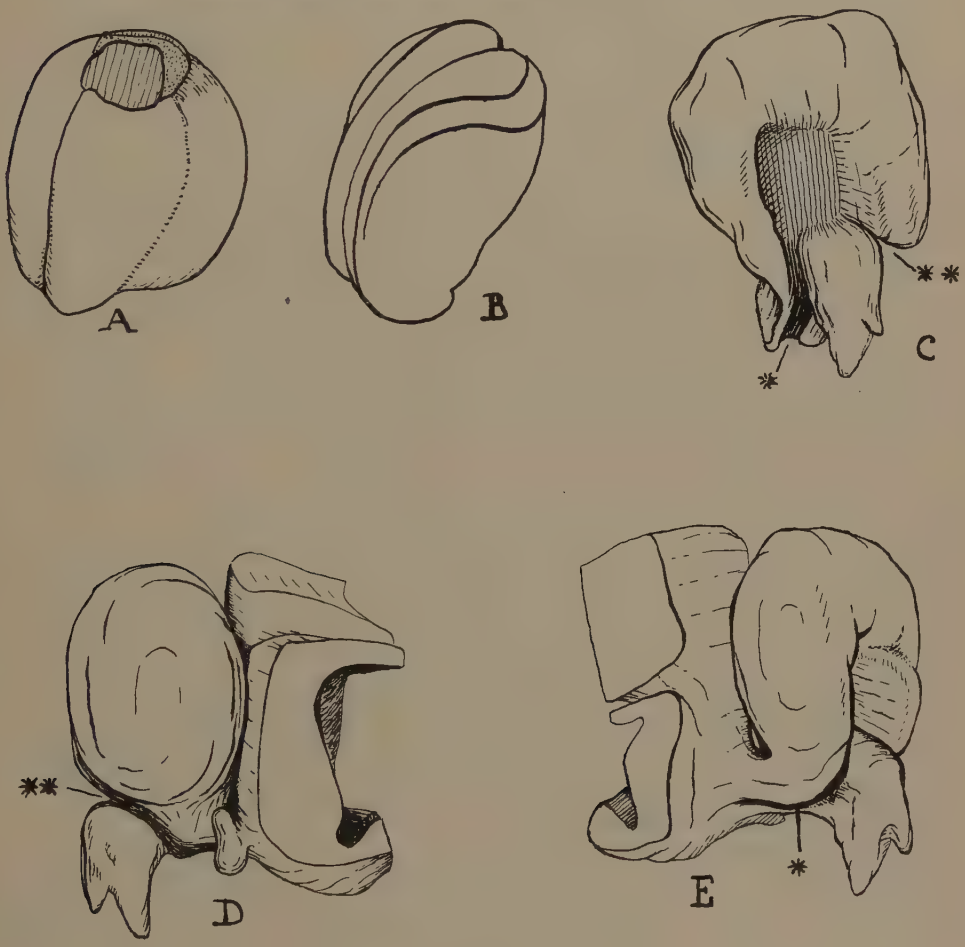


Abb. 3.

war von der Operation nichts mehr zu sehen (Abb. 3 *B*), das Neuralrohr hat sich nachher normal geschlossen.

Bei der Untersuchung des operierten Auges stellte sich heraus, dass es zwei Augenspalten besass. In Abb. 3 C sieht man das Auge (rechts) von lateral (Wachsplattenrekonstruktion). Es besitzt eine ventrale Spalte, die sich auf den Augenstiel fortsetzt (*), und eine zweite, die nach vorn

und ventral gerichtet ist (**). Die letztgenannte setzt sich auch auf den Augenstiel fort, sie ist die herkunftsgemässe Spalte; die ventrale dagegen ist die ortsgemässe. In Abb. 3*D* sieht man die Augenanlage von vorn und kann man die Fortsetzung der herkunftsgemässen Spalte auf dem Augenstiel sehen. In Abb. 3*E* sieht man das Auge von hinten und von rechts.

Aus diesen und ähnlichen, nicht abgebildeten, Fällen geht also hervor, dass schon in der Neuralplatte die Richtung der Augenspalte bei meinen Versuchsobjekten (Triton taeniatus, Rana esculenta und Axolotl) determiniert war. Nach Drehung der Augenplatte kann sich die Spalte nämlich herkunftsgemäss entwickeln. Aber unter Einfluss von Umgebungsfaktoren kann ihre Richtung auch derart abgelenkt werden, dass sie mehr oder weniger ortsgemäss verläuft oder geknickt wird. Schliesslich kann sich neben der herkunftsgemässen Spalte eine ortsgemässe entwickeln.

Ich komme also zu ähnlichen Ergebnissen wie SATO. Aber SATO arbeitete mit älteren Stadien, und seine Untersuchung gab keinen Aufschluss über die Determination der Augenspalte in der Augenplatte.

Wir sehen, dass selbst, wenn die Augenplatte ohne Unterlagerung gedreht wird, herkunftsgemässe Entwicklung der Augenspalte möglich ist. Es müssen deshalb wohl in der Augenplatte schon Wachstumsrichtung und Einstülpungstendenzen des Auges determiniert sein. Die Determination ist aber eine labile.

Das Entstehen normaler Augen aus der gedrehten Anlage weist darauf hin, ebenso wie die Ablenkung der Augenspaltenrichtung.

Aus SATO's Untersuchungen geht hervor, dass *die Determination während längerer Zeit labil bleibt.* Das ist auch meine Erfahrung, denn nach Umschneidung der sich vorwölbenden Augenblase und Drehung um 90° habe ich in manchen Fällen normale Entwicklung des Auges bekommen, d.h. mit ortsgemässer Augenspalte (Rana).

In der Umgebung der Augenanlage wirken Faktoren, die eine ortsgemässe Spaltenentwicklung bei gedrehten Augenanlagen bewirken können. Ihre Wirkung ist es wahrscheinlich, wodurch bei normaler Entwicklung die labile Determination fixiert wird.

Diese Fixierung findet aber offenbar erst statt bei der primären Augenblase.

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Psychology. — *Children of the happily and unhappily married.* By E. D. WIERSMA. (Second article.)

(Communicated at the meeting of November 24, 1934).

Having previously [1]) thrown light on the distinction between the happily and unhappily married, we shall consider in this article whether there is any relation between the conjugal happiness of the parents and the mental condition of the children, in other words, whether any differences may be pointed out between children of happily and unhappily married parents. For this research also the heredity inquiry has been used. The number of children considered amounts to 1607, 70.9 % of which originate from happily married, 9.7 % from unhappily married, and 19.4 % from parents about whose conjugal happiness no judgment was given. The number of children from each marriage amounts on an average to 3.6, from each happy marriage to 3.5, from each unhappy marriage to 3.4. According to these data conjugal happiness has hardly any or no influence at all on the number of children. The investigation of this material comprises the same headings as the preceding article [1]).

I. LIST OF PERCENTAGES.

	Children of		
	Happy marriages	Unhappy marriages	All marriages
1. Restless and vivacious	43	42	44
Calm and quiet	52	51	50
2. Constantly diligent	73	60	66
By fits and starts	17	25	21
Lazy	7	10	9
3. Usually busy	59	55	55
Take things easily	32	34	36
4. Neglect	13	19	16
5. Delay	31	38	35
Tackling things	54	51	50
6. Easily discomfited	25	30	25
Persevering	48	36	40
Stubborn	13	26	20
7. Impulsive	38	44	42
Level-headed	45	40	41
Man of principle	4	5	5

[1]) Verhandelingen der Koninklijke Akademie van Wetenschappen. XXXIV, N°. 1.

	Children of		
	Happy marriages	Unhappy marriages	All marriages
8. Resolute	53	59	53
Irresolute	27	33	29
9. Emotional	53	56	53
Not emotional	35	36	35
10. Violent	43	45	45
Cool and business-like	39	38	37
11. Irritable	38	50	43
Unable to get angry	2	3	2
12. Critical	41	19	31
Idealizing	30	29	28
13. Suspicious	20	26	21
Credulous	43	35	39
14. Tolerant	81	63	73
Intolerant	8	13	11
15. Merry and cheerful	41	32	37
Sombre	5	5	4
Both by turns	30	40	34
Calm and equable	20	20	20
16. Gloomy	27	29	27
Light-hearted	39	30	39
17. Easily consoled	37	40	36
Grieving for a long time	20	17	20
18. At once reconciled	43	36	41
Put out for some time	31	39	35
Difficult to conciliate	12	19	15
19. Variable in sympathy	19	30	23
Constant in affections	66	64	64
20. Attached to old memories	47	37	41
Taken up by new impressions	27	32	29
21. Clinging to opinions once formed	22	24	23
Open to new views	53	46	47
Easy to talk round	11	15	14
22. Fond of change	38	44	41
Man of routine	36	35	31
23. Repeatedly	7	10	9
Never	52	44	46
Once having left one business	11	7	9
24. Great plans	48	51	48
25. Thoughts of a distant future	30	41	34
Of immediate results	32	34	33
26. Actions in agreement	64	54	60
In contradiction with principles	12	20	15
27. Quickness of mental grasp	57	54	57
Intelligent	49	46	46
Superficial	18	24	20
Stupid	3	7	5
28. Good judge of human nature	45	38	39
Not	24	36	30

	Children of		
	Happy marriages	Unhappy marriages	All marriages
29. Practical	67	69	67
Unpractical	16	20	19
30. Broad-minded	63	55	58
Narrow-minded	18	29	22
31. Independent	63	58	61
Repeat what others say	21	26	23
32. Definite opinions	52	54	51
Conditionally	20	27	22
33. Talent for mathematics	13	10	10
Languages	13	11	11
Music	17	19	19
Drawing	8	6	8
Literary work	8	6	7
Acting	5	5	6
Imitating people	9	9	10
34. Witty	40	46	43
Not witty	29	37	31
35. Conversable	67	56	63
Monopolize the conversation	7	12	9
Quiet and reserved	17	26	19
36. Good narrator of anecdotes	21	27	23
Longer stories	14	15	16
Self-made stories	9	13	11
37. Long-winded	14	24	18
Concise	54	55	54
38. Tell the same stories	9	11	9
39. Speak in public	17	14	16
Do not	43	51	45
40. Good observer	56	56	54
Not	15	27	20
41. Very good ear for music	15	15	17
Good	48	56	49
Poor	26	18	21
42. Handy	57	59	58
Unhandy	13	22	17
43. Exceptionally good memory	11	9	10
Good	77	76	73
Bad	5	9	9
44. Fond of good things to eat and drink	40	35	40
Not	35	41	36
45. Drunkard	1	0	0
Regularly	9	8	9
Now and again	47	33	41
Never taking alcohol	19	20	19
46. Dissolute in sexual matters	6	10	7
Continent	60	60	56
47. Satisfied with his own capabilities	31	40	36
Not satisfied	36	37	35

	Children of		
	Happy marriages	Unhappy marriages	All marriages
48. Vain and coquettish	22	30	28
Not	48	38	40
49. Ambitious	32	36	36
Indifferent	26	26	25
Inclined to keep in the background	19	17	16
50. Covetous	15	29	21
Not covetous	50	45	48
51. Avaricious	1	5	3
Thrifty	45	44	44
Liberal	46	33	39
Extravagant	6	16	12
In debt	2	6	5
52. Domineering	20	28	23
Inclined to give each his freedom	53	48	50
Easily led	13	11	12
53. Stern towards children	5	7	5
Tender and solicitous	24	20	21
Give them great liberty	8	8	9
54. Good to his servants	81	79	77
Not good	5	6	6
55. Compassionate	69	60	64
Egoistic	11	27	18
56. Active and philanthropic	21	18	19
Financial support	29	26	27
Not	10	21	14
57. Radical in politics	16	16	14
Moderate	24	24	23
Conservative	8	8	8
Indifferent	21	26	25
58. Active part in politics	5	7	5
Not	56	56	58
59. Warm patriot	27	14	19
Not	30	41	35
60. Quite natural	69	54	60
Forced	18	31	24
Affected	7	12	10
61. Demonstrative	32	40	35
Close	46	42	43
62. Admitting his intentions	71	68	69
Diplomatic	14	17	17
Intriguer	2	6	3
63. Strictly credible	64	54	59
Exaggerating	18	29	22
Embellishing	11	19	15
Mendacious	3	7	5
64. Absolutely reliable	80	74	75
Honest within the limits of the law	6	14	9
Dishonest	1	2	2

	Children of		
	Happy marriages	Unhappy marriages	All marriages
65. Ardently religious	19	10	14
Conventional	19	19	17
Ridiculing	5	14	7
Indifferent	28	53	44
66. Fond of children	66	64	64
Not	10	19	14
67. Fond of animals	52	53	50
Not	20	24	20
68. Inclination to higher	19	23	22
To lower standing	10	16	13
69. Different in tone	8	18	11
Alike to all	77	73	75
70. Courageous	46	53	47
Fearful	30	34	31
Cowardly	1	4	3
71. Fond of going out	26	24	27
Domesticated	54	56	52
Solitary by nature	8	14	10
72. Talking of business	36	29	31
Of persons	19	25	22
Of himself	7	19	13
73. Fond of sexual jokes	14	28	20
Averse from them	46	43	43
74. Reading a great deal	50	49	48
Little	35	37	36
Accurately	45	46	44
Inaccurately	13	25	18
75. Abstract meditations	16	20	18
76. Zealous collector	10	10	11
77. Neologisms	14	11	13
78. Lover of sport	48	51	48
79. Fond of intellectual games	30	26	26
80. Of games of chance	8	9	10
For large stakes	2	2	2
81. Acquainted with family relations	18	23	19
82. Complimentary	7	10	9
Ordinarily polite	83	83	82
Grumbler	4	6	4
83. Absent-minded	22	32	27
Always awake	52	52	50
84. Neat	66	72	68
Careless	23	20	21
85. Accurate	66	63	62
Not	19	25	26
86. In speech important	8	13	10
Business-like	31	29	27
Bon enfant	36	42	38
Swaggering and blurting	15	16	14
Ironical	9	11	8

	Children of		
	Happy marriages	Unhappy marriages	All marriages
87. In tone drawling	5	5	5
Shouting	7	10	8
Prattling on	52	62	51
Clipping his words	9	8	10
88. Laughing a great deal	41	40	40
Little	40	39	35
Never	1	0	0
At his own jokes	4	8	6
89. Courageous when ill	36	35	35
Afraid	23	33	26
Patient	36	31	35
Impatient	21	27	22
Speedily calling in medical assistance	30	33	31
Not	18	20	19
90. Having suffered from psychical aberrations	15	15	17

II. Differences in temperament

1. *Simple temperamental qualities.*

The following table gives a synopsis of the average percentages of activity and non-activity, of emotionality and unemotionality, of the secondary and primary function of the children of happily, unhappily, and all married people.

	Children of		
	Happily	Unhappily	All married people
A	67	63	66
nA	26	34	29
E	53	56	53
nE	35	36	35
S	55	49	53
P	33	38	34

According to this table the children of the happily married are a little more active and less non-active, a little more secondary and less primary than the average, whereas the children of the unhappily married are somewhat less active and more non-active, somewhat less secondary and

more primary than the average. With regard to the emotionality and unemotionality the differences are very inconsiderable. The temperamental qualities of the children consequently deviate from the average in the same direction, though in a minor degree, as those of their parents.

2. *Compound temperamental qualities.*

α. Activity and psychical after-effect.

Children of

	Happily	Unhappily	All married people
AS	38	36	38
AP	17	19	17
nAS	9	8	9
nAP	15	18	16

The children of the unhappily married are somewhat less active secondary and somewhat more non-active primary than the average. Consequently they display resemblance to the non-active primaries, in the same way as their parents, though less conspicuously. The children of the happily married hardly deviate from the average.

β. Activity and emotionality.

Children of

	Happily	Unhappily	All married people
AE	36	35	35
AnE	20	22	21
nAE	14	19	15
nAnE	9	13	10

Most striking is the approach of the children of the unhappily married to the non-active emotional and non-active unemotional. In this connection they agree with their parents. The children of the happily married differ little from the average.

γ. Emotionality and psychical after-effect.

	Children of		
	Happily	Unhappily	All married people
ES	26	21	25
EP	20	24	20
nES	20	19	20
nEP	10	9	10

It is evident that the children of the unhappily married are more emotional primary and less emotional secondary than the average and than the children of the happily married, and that in this respect they resemble their parents.

3. Types of temperament.

	Children of		
	Happily	Unhappily	All married people
Phlegmatic AnES	17	10	15
Sanguine AnEP	4	3	4
Passionate AES	20	14	20
Choleric AEP	10	10	10
Sentimental nAES	4	4	4
Nervous nAEP	8	13	8
Apathic nAnES	3	5	3
Amorphous nAnEP	4	5	5

The children of the unhappily married are less sanguine and considerably less phlegmatic and passionate, more apathic and amorphous and considerably more nervous than the average and than the children of the happily married. Consequently also with regard to the types of temperament there is a great similarity between parents and children.

III. Conjugal happiness of the parents and the intellect of the children.

As we have seen, the intellect of the happily married comes up to a higher level, of the unhappily married to a lower one. Are indeed the

children of the happily married, in the same way as their parents, characterized by greater quickness of mind and level-headedness, the children of the unhappily married by a lowered degree of consciousness?

1. *Intellectual advantage.*

We here distinguish persons who are quick of mind and the level-headed. Both forms are met with in a greater number in children of the happily married than in children of the unhappily married. With regard to quickness of mind this appears from the wider mental grasp (27) and from the greater accessibility to new views (21); with regard to level-headedness from the higher degree of intelligence (27), of knowledge of human nature (28), of broad-mindedness (30), of independence of thought (31), of the development of talents: mathematics, languages, literary work (33). On the other hand the children of the happily married are surpassed by the children of the unhappily married in some qualities, such as practical sense (29), telling of longer and self-made stories (36), and conciseness in narration (37).

The average percentages of the intellectual advantage are for all children 37.2 %, for children of the unhappily married 36.6 %, for children of the happily married 39.1 %. Quickness of mind and level-headedness are, therefore, found in children of the happily married more, in children of the unhappily married a little less than the average.

2. *Intellectual inferiority.*

The intellectual inferiority, due to a lowered degree of consciousness, exhibits the rudimentary phenomena of the various forms of dementia. More than the average and more than in the happily married this inferiority is found in the unhappily married. How is in this respect the state of affairs in the children of the unhappily married? Do they, in the same way as their parents, exhibit similarity, though in a very elementary form, to the much stronger disturbances in adaptation and mental grasp of normal old age and senile dementia, to the association disturbances as they are found in pathological form in paralytic dementia, and to the non-active absent-mindedness which may be pointed out in a highly increased form as primary phenomenon in nearly all epileptic patients?

With regard to the similarity to the mental decay of old age, the mental grasp (27) appears to be slighter and consequently the exceptionally good memory deteriorated and the bad memory (43) worse, the long-windedness and prolixity in narration increased (37), repetition of the same stories more frequent (38), clinging to established opinions increased (21), accessibility to new views diminished (21), annoyance after a fit of anger longer (18), the difficulty to be reconciled and to dismiss the thought of the affect, which causes a grudge to remain against particular persons

(18) greater, while the obstinacy making them less accessible to advice from others and inducing them to persist in having their way against their better knowledge (6), has increased.

The average percentages, indicating a decreased adaptability, amount for children of the happily married to 15.1 %, for the children of the unhappily married to 21.7 %, and on an average to 18.4 %. Consequently the phenomena of reduced mental suppleness and of greater rigidity, characteristic of normal old age and of senile dementia, are found in the children of the unhappily married, as well as in their parents, to a larger extent than the average and than in the children of the happily married.

Reduced associative activity, the diminished capacity to form associations, characterizing paralytic dementia, is met with in the children of the unhappily married, it is true in mitigated form, but yet to a larger extent than the average and than in the children of the happily married. They are more superficial and stupid (27), possess less knowledge of human nature (28), are more unpractical and incapable to help themselves (29), they overrate their own achievements (47), are inclined to put themselves in the foreground by monopolizing the conversation in company (35), they are prolix and long-winded in their stories (37), unhandy (42), less independent and inclined to repeat what others say (31), they are easy to talk round (21), their actions are usually aimed at obvious results (25) and frequently contrary to previously expressed principles (26). On at average the percentages of the qualities indicating a weaker associative activity and judgment amount in children of the happily married to 16.8 %, in children of the unhappily married to 23.3 %, and averagely 19.9 %, so that the intellectual inferiority in this form in the children of the unhappily married is greater, in children of the happily married less than the average.

The increased lability of attention, characteristic of the epileptics and expressed most strongly in these patients in the so-called epileptic character, becomes manifest by a greater degree of absent-mindedness and a smaller activity. With regard to these primary symptoms there exists an approach to this form of mental sinking-in in the children of the unhappily married, as well as in their parents. They are more absent-minded (83) and less active (2, 3 and 5) than the average and than the children of the happily married. The intellectual qualities also display this similarity. The retarded process and the lowered degree of the psychical functions are apparent from the slow mental grasp (27), the great narrow-mindedness (30), the low degree of independence (31), the forced and affected manner (60), the tendency to exaggerate and to embellish stories (63), the habit of speaking by preference of themselves (72), excessive politeness and abundant compliments (82), the high degree of obstinacy (6), the increased irritability (11), and from the great fluctuations in mood (15). The average percentages of the psychical qualities of labile attention or non-active absent-mindedness amount averagely to 22.7 %, for children of the happily married to 18.5 %, and for children of the

unhappily married to 25.7 %. In this respect also the children of the happily and of the unhappily married deviate from the average in the same direction as their parents.

IV. Conjugal happiness of the parents and the tendencies of the children.

1. *Vital tendencies.*

α. Physical needs.

The tendency of children of the unhappily married to satisfy their physical needs more eagerly, which would show their greater weakness of will, is no rule. In some qualities they appear to be more moderate. This holds good for fondness of good food and drink (44), the desire for alcohol (45). In sexual matters, however, they are more dissolute (46) and fond of sexual jokes (73). The children of the happily married are less averse to the pleasures of the table (44) and alcohol (45). Sexually they are less dissolute (46) and more averse to sexual jokes (73). In the eagerness and moderation to fulfil physical needs, therefore, there is no perfect agreement between parents and children.

β. Mental needs.

We have made a distinction between passive and active observers. With respect to these tendencies also there is a difference between the children and their parents. In fondness of going out or retirement (71), in the habit of reading much or little (74), the differences between the two groups of children and the deviations from the average are very slight. Surrendering to abstract meditations (75), indulgence in games of hazard (80), for which little or no exertion is wanted, is found more than the average in children of the unhappily married. On the other hand accurate reading and the exact rendering of what has been read (74), the practice of intellectual games (79), the ability to keep others pleasantly occupied (35), yield satisfaction to the mental needs by the continual intellectual exertion. These qualities are found more than the average in children of the happily married. This is not the case with the collection of objects (76), practice of sports (78), the tracing of family relationships (81), for which evidently not sufficient intellectual exertion is demanded to satisfy the children of the happily married. The children of the happily married, therefore, are more than the average satisfied, though not so regularly as their parents, by the active exertion of the attention, whereas the children of the unhappily married are satisfied more than the average by the passive indulgence in distractions which chance to offer.

2. *Egophils.*

In *haughtiness* the children of the unhappily married exceed the average. They are satisfied with their own achievements (47), vain and coquettish (48), they try to associate with persons of higher or of lower standing (68), prefer to talk about themselves (72), laugh mainly at their own jokes (88). The children of the happily married are in all these qualities and also in ambition (49) below the average. They show greater *modesty*, rising in this respect above the average. They possess a higher degree of selfcriticism (47) than the average, they are less vain and coquettish (48), less ambitious and more inclined to keep in the background (49), they talk more about things and less about persons and themselves (72), they laugh less at their own witticisms (88).

Covetousness is found to a greater extent than the average in children of the unhappily married, to a less extent in children of the happily married. The former are more covetous (50), avaricious (51), extravagant and consequently more frequently in debt (51). *Non-covetousness* on the other hand is greater than the average in children of the happily married. They are more non-covetous (50), more thrifty, but under circumstances, also more liberal (51).

Arrogant presumption is found more than the average in children of the unhappily married, less than the average in children of the happily married. the former are more domineering (52), have a louder tone of voice (87), are different towards their superiors and those below them (69), have more definite opinions (32), and are more demonstrative (61). The children of the happily married are *less pretentious*. They leave each his freedom and are easily led (52). They behave less differently towards superiors and subordinates (69), are less decided in their expressions (32) and less demonstrative (61) than the children of the unhappily married.

In the same way as the unhappily married parents their children are haughtier, more covetous, more arrogant, and similarly to the happily married parents their children are more modest, less covetous, less pretentious than the average.

3. *Altruists.*

Family feeling in the form of tenderness and care for their children (53), a *friendly disposition* towards servants and subordinates (54), *compassion and helpfulness* (55), *philanthropic activity* (56), *patriotism* (59) are in children of the happily married above the average, in children of the unhappily married below it. Consequently in this respect also there is a similarity between parents and children.

4. *Abstract tendencies.*

The children of the happily married are above the average in *sense of duty*: they are accurate and conscientious in their work (85), in the habit

of tackling and finishing everything energetically (5); *in truthfulness*; they honestly admit their intentions (62), tell their stories without embellishments (63); in *honesty and reliability*: they keep their engagements and act in accordance with the principles they express (26), they are absolutely reliable in money affairs (64); in *tolerance*: they idealize their fellow-men (12), are credulous (13) and tolerant (14); in *self-importance*: they resolutely persist in their opinions with a sense of their own worth (6); in *courage* in danger (70) and illness (89) the deviation from the average is only slight and this also applies to determination (8); in *steadfastness*: they are always ready with an independent opinion and do not let themselves be talked round by others (31); in *unaffectedness*: they are natural in manner (60), polite, without exaggeration (82), they speak in a matter-of-fact or in a good-natured manner (86). The children of the unhappily married on the other hand are below the average in *sense of duty*: they do not keep their engagements (85), neglect compulsory work (4); in *truthfulness*: they conceal their intentions diplomatically (62), they dissemble and intrigue, sometimes by making use of unfair means (62), they are inclined to embellish their stories and to tell lies (63); in *honesty and reliability*: they often act contrary to promises and agreements (26) and are frequently only honest within the limits of the law or even dishonest (64); they are above the average in *intolerance*: they are suspicious (13), intolerant (14); in *fearfulness*: they are afraid and cowardly in danger (70), fearful and impatient in sickness, soon call in medical assistance (89); in less *self-importance*: they are quickly discouraged (6), act impulsively or according to previously fixed principles (7) or sometimes they are hesitating and irresolute (8); in *pessimism*: they are gloomy (16); in *suggestibility*: they are inclined to repeat the opinions of others (31), are easy to talk round (21), cling obstinately to previously conceived opinions (6); in *affectation*: they are more or less forced or affected (60), complimentary or grumbling, irritable and peevish (82), and have a swaggering and ironical (86) manner of speaking.

In the children of the unhappily married as well as in their parents the higher tendencies are on a lower level, the lower tendencies on a higher level, whereas in the children of the happily married the higher tendencies are found to a greater extent, the lower tendencies to a less extent than the average.

Recapitulating we find that there is a similarity between the children of the unhappily married and their parents and between the children of the happily married and their parents as far as temperament, intellect, and most tendencies are concerned. This similarity is not so complete with regard to the satisfaction of physical and mental needs.

Physics. — *Continued investigations on the luminescence and crystal structure of solidified gases.* By L. VEGARD. (Communicated by Prof. W. H. KEESOM).

(Communicated at the meeting of November 24, 1934).

§ 1. *The luminescence from solid krypton containing traces of nitrogen.*

When highly purified solid argon is bombarded with electric rays, the very bright luminescence is dominated by the vibrational series which we call ϑ and δ; and in certain cases also the series π, χ, ψ, and ε were observed. These series are no doubt due to the small quantities of impurities contained in the argon, and not to argon itself. This view was supported by the fact that certain lines emitted from solid neon nearly coincided with lines of the δ-series, and that the N_1 and N_2 bands, which are shown to originate from nitrogen, also appeared in the argon luminescence. In order to settle the question it would be of interest to study the luminescence of other solidified inert gases, and during the last year we have made experiments with solidified krypton.

The luminescence produced when solid krypton is bombarded with cathode rays was examined in two series of experiments undertaken in Febr. 1932 and March 1933. By the first experiment we obtained with our quartz spectrograph a spectrogram shown on plate No. 1. The bands thus obtained are given in Table I, and most of them belong to the ε-system. The estimated relative intensity is indicated to the left of the wave-length number in an arbitrary scale 1—5.

We have previously seen that the ε-system appearing in the neon-nitrogen mixtures was not quite identical with that of argon-nitrogen. In neon-nitrogen each band was split up in a larger number of components, and none of these were perfectly coinciding with either of the two components observed from argon-nitrogen mixtures. In the case of krypton the bands show no multiple structure at all. In the second column of Table I we have given the corresponding "ε-doublets" observed from argon-nitrogen mixtures, and we notice that the single "krypton" band nearly corresponds to the weaker component of the "argon" doublets. This may also mean that the ε-bands in krypton are displaced towards longer waves with respect to the ε-bands of argon. The displacement amounts to about 40 cm^{-1}.

By an experiment carried out in March 1933 spectrograms were taken with a large glass spectrograph on pancromatic plates, one of which is reproduced on plate No. 2. These spectrograms show a number of quite

TABLE I.

"Pure" Krypton.

"Pure" Krypton		ε-system in Argon-N_2 Mixtures	Interpr.	"Pure" Krypton		ε-system in A-N_2 mixtures	Interpr.
5 d.	5577.9		N_1	5	2953.3	2952.3 2947.0	ε (0.7)
2	4691.9			1?	2902.9	2898.2 2895.9	ε (5.10)
2	4524.9	4511.71	ε (6.17)	3	2833.7	2832.6 2827.3	ε (1.7)
2	4298.6	4298.76 4290.85	ε (4.15)	5	2776.5	2774.8 2770.4	ε (0.6)
4	4219.0			1	2737.9	2736.6 2732.5	ε (5.9)
2	4099.5	4096.04 4089.99	ε (2.13)	3	2724.8	2722.9 2719.2	ε (2.7)
2	4007.5	4001.56 3995.65	ε (1.12)	2	2681.3	2679.6 2675.7	ε (4.8)
3	3940.1			3	2644.7	2641.2 2639.3	ε (6.9); ×
4	3867.4	3860.8	ε (6.15)	5	2617.9	2616.1 2612.5	ε (0.5)
2	3791.6	3789.8 3784.9	ε (2.12)	2	2574.3	2571.7 2568.7	ε (2.6)
3	3708.3	3709.7 3701.0	ε (1.11)	2	2537.3	2534.6 2531.5	ε (4.7)
2	3689.9	3681.1	ε (4.13)	d. max	2534.5		×
2	3625.4	3627.0 3619.7	ε (0.10)	3	2524.2	2521.7 2518.3	ε (1.5)
3	3599.4	3600.5 3594.0	ε (3.12)	3	2506.1	2501.3	ε (6.8)
3	3523.3	2522.5 2517.8	ε (2.11)	5	2475.2	2472.8 2469.2	ε (0.4)
2	3494.4			1	2454.9	2451.8 2449.7	ε (5.7)
1	3469.4			d. max	2419.7		×
4	3448.0	3446.8 3440.3	ε (1.10)	3	2390.8	2388.0 2385.5	ε (1.4)
2	3386.3			1	2358.2	2355.2 2353.2	ε (3.5)
3	3373.3	3371.9 3366.8	ε (0.9)	3	2345.1	2343.0 2340.2	ε (0.3)
2	3287.2	3285.4 3281.8	ε (2.10)	1	2287.5	2283.0 2281.0	ε (4.5)
4	3217.9	3217.2 3211.3	ε (1.9)	2	2270.1	2267.5 2265.1	ε (1.3)
4	3152.2	3148.8 3144.0	ε (0.8)	1	2264.3	2258.0	ε (6.6)
4	3015.0	3012.0 3008.3	ε (1.8)	1	2228.0	2226.2 2223.6	ε (0.2)
3	2966.2	2961.5	ε (6.11)				

sharp lines, the wave-lengths of which are given in the first column of Table II.

TABLE II.

"Pure" Krypton,

"Pure" Krypton	"Pure" Argon	Interp.	"Pure" Krypton	"Pure" Argon	Interpr.
1 d. 6711.1	6710.5	σ_4^0	1 d? 5388.0		
2 6656.5	6653.5	ϑ_5^2	1 d. 5362.9		
1 6595.7			1 5334.9		
1 d. 6497.6			2 5252.9		ε (5—18)?
1 d. 6409.5			2 5241.2	5239.5	
2 6316.7		ψ_7^1	3 5225.2	5224.6	N_2
5 6046.4	6043.5	ϑ_4^2	1 5207.5	5209.0	
1 6016.2	6014.3	ϑ_4^0	1 5194.1		
2 5990.5			3 5179.2	5178.7	ψ_5^1
3 d. 5939.2			2 d. 5114.2	5109.3	$\sigma_1^1 - \varepsilon$ (4.17)
1? 5818.3			5 5086.0	5080.9	ϑ_2^2
1? 5777.1	5776.4		1 4756.9	4754.4	ψ_4^2
3 5756.5			1 4750.4		
1? 5714.0	5714.8	ψ_6^2	3 4743.2	4743.5	ψ_4^1
4 d. 5694.3	5695.8	ψ_6^1	2 d. 4723.9	4718.8	σ_0^1
5 d. 5627.3	5622.3	N_1 (b)	2 4709.5	4706.5	σ_0^0
1 5568.7	5563.7	σ_2^1	5 4704.1		ϑ_1^2
5 5528.8	5525.3	ϑ_3^2	1 d. 4681.5	4681.6	ϑ_1^0
1 5455.0			2 4671.7		
1 d. 5418.5			2 4371.7		ϑ_0^2

The second column contains corresponding bands observed from argon. We notice that the most conspicuous lines of the krypton spectrum are identical with lines of the ϑ, δ and ψ series and with the N_1 and N_2 bands. This result shows that the series ϑ, δ and ψ do not originate from the inert gas, but from a common impurity which is difficult to remove from the inert gas.

The large vibrational frequency of these bands shows that they originate from a substance, which in the solid state has a molecular structure. Among the elementary gases only oxygen, hydrogen and nitrogen deserve consideration. Now the first two elements are easily removed and hydrogen is

not solidified at the temperature used. The presence of the N_1, N_2 bands shows that the krypton and argon contain nitrogen and the δ, ϑ series are no doubt to be referred to nitrogen.

§ 2. *The infra red luminescence from solid nitrogen and its mixtures with argon.* –

For the investigations of the infra red luminescence we at first used a plate Agfa infra red (810 $\mu\mu$) and later on we used Agfa infra red (700—900 $\mu\mu$). The plates were hypersensitized with a solution of ammonia. Spectra on infra red plates were obtained for the following systems: "Pure" argon, argon + 3.5 % nitrogen, and pure nitrogen. For each system spectrograms were taken from the direct luminescence, during ray bombardment, and also from the afterglow. Some typical spectra are given on the plate Nos. 3—9. The experimental conditions corresponding to each spectrogram are given in the explanation to the plates at the end of the paper.

The observed infra red lines and bands for the three systems mentioned are given in Table III. Those appearing in the afterglow are denoted by

TABLE III.

Bands and lines in infra red.

"Pure" Argon	A + 3.5% N_2	Pure N_2	"Pure" Argon	A + 3.5% N_2	Pure N_2
1 9086				1 d? (7775)	
2 8972			4 br. 7750	3 d. 7750	
1 d. 8687			1 7629		
		1 8648		1 d. 7530	
	2 8562	5 8562	1 7440		
3 8469	3 8464	2 d. 8475	2 d. 7370	1 d. 7368	
1? (8427)			4 7241	4 7243	
	1 8370		2 d. 7188		
	1 8292		1 d. 7123	1 d. 7126	
4 8273			2 d. 6899	2 d. 6869	
4 8201			2 d. 6824		
	2 d. 8176		2 d. 6679	2 d. 6673	
5 8056	5 8069			1 d. 6442	
	2 8000	2 d. 8004	1? (6357)		
	3 7937	5 7925			
3 7857					

heavy types. The relative intensity is indicated by numbers (1—5) to the left of the wave-length value. We notice that only two bands $\lambda = 8002$ and $\lambda = 7930$ appear in the afterglow, but these bands do not at all appear on the spectrograms from "pure" argon. The infra red bands appearing in het afterglow originate from solid nitrogen. The quantities of nitrogen present in the purified argon are too small for these bands to appear with any noticeable intensity.

We have not been able to classify any of the infra red bands into new vibrational series or to refer them to series known from previous investigations.

§ 3. *The structure of β-nitrogen and the different phosphorescent power of the α- and β-form.*

The results of our determination of the crystal structure of β-nitrogen and their relation to the explanation of the phosphorescence properties of solid nitrogen have been described in a paper recently published. [1])

In this paper we gave an account of the experimental procedure and the considerable difficulties which had to be overcome. After having tried various experimental arrangements we finally constructed a cryostat with *X*-ray camera which made it possible for us to obtain powder diagrams of solid β-nitrogen. This diagram was interpreted by means of a hexagonal elementary cell, with an axis proportion $c/a = 1.651$ and $a = 4.039$ Å. The cell contained two molecules, and from the dimensions of the cell we found for β-nitrogen the density $\zeta = 0.982$. This result is in good agreement with a result obtained independently by M. RUHEMANN [2]), who found $c/a = 1.633$ and $a = 4.034$ Å. This agreement is the more remarkable as our experimental arrangements differed very essentially.

For the question as to the possible relation between the crystal structure and the phosphorescence of solid nitrogen, it was essential not only to determine the unit cell, but to find the position of the atoms. A discussion of the possible space groups on the basis of the intensity distribution of our powder diagram led to the somewhat startling result, that the individual atoms do not occupy definite positions in accordance with the point arrangement of a certain space group. The molecular elements were found to diffract the *X*-rays as if both atoms were situated at the centre of the molecule. That means that the directions of the molecular axes are irregularly distributed. Such an irregular distribution of the molecular axes is most simply explained if we assume that the molecules rotate in the lattice. *Thus we can describe the structure of β-nitrogen as a hexagonal close packing of rotating molecules.*

In the α-form of nitrogen the atoms are fixed on trigonal axes according to the space groups T_4. [3]) The molecular axes here have fixed positions

[1]) L. VEGARD. Z. S. f. Phys. **79**, 471, 1932.
[2]) MARTIN RUHEMANN. Z. S. f. Phys. **76**, 368, 1932.
[3]) L. VEGARD, Z. S. f. Phys. **58**, 497, 1929.

in the crystal lattice. Regarding the arrangement of the molecular centres in α-nitrogen, we find that they are approximately arranged in a face-centred lattice, which would mean an arrangement of the closest cubical packing.

If in both modifications the molecules were to be regarded as spheres with the same radius, we should expect both forms to have the same molecular volume. We find, however, that the β-form has a molecular volume of 47.12 10^{-24} cm^3, which is considerably larger than that of α-nitrogen (45.33 10^{-24} cm^3). We see that the rotating molecules of the β-form require more room than the non-rotating molecules in the α-form. The rotation of the molecular elements of β-nitrogen also explains the fact that the intensity of the X-ray reflections diminishes so rapidly with increasing angle of deviation.

§ 4. *Phosphorescence and crystal structure.*

In previous papers accounts were given [1]) of a large number of vibrational series and systems appearing in the luminescence from solid nitrogen and its mixtures with inert gases, and at the same time we tried to group the series into families and to find the electronic transitions engaged in the formation of each family. In the case of the ε-system to which may also be referred the B, b, D, d, F, f, and probably the $\varkappa$-series, we were able to determine the vibrational terms with great accuracy. The ε-system as it appears in argon-nitrogen mixtures is given by the following formula:

$$\nu = a + T'(n_1) - T''(n_2)$$

where:

$$T''(n_2) = 2353{,}1\ n_2 - 14{,}9\ n_2^2$$

$$T'(n_1) = 1453{,}1\ n_1 - 14{,}9\ n_1^2$$

$$a_1 = 49670\ cm^{-1}$$

$$a_{II} = a_I - 45{,}4\ cm^{-1}.$$

The vibrational term of the lower ε-state is identical with that of the normal nitrogen molecule as derived from the ultra violet N-bands, for which the following vibrational term is found:

$$2345{,}1\ n_2 - 14{,}4\ n_2^2.$$

The vibrational term of the upper ε-state is identical with the A-state forming the lower state of the lst. positive group of nitrogen. The vibrational term of the A-state is found to be:

$$1446{,}5\ n_2 - 13{,}93\ n_2^2.$$

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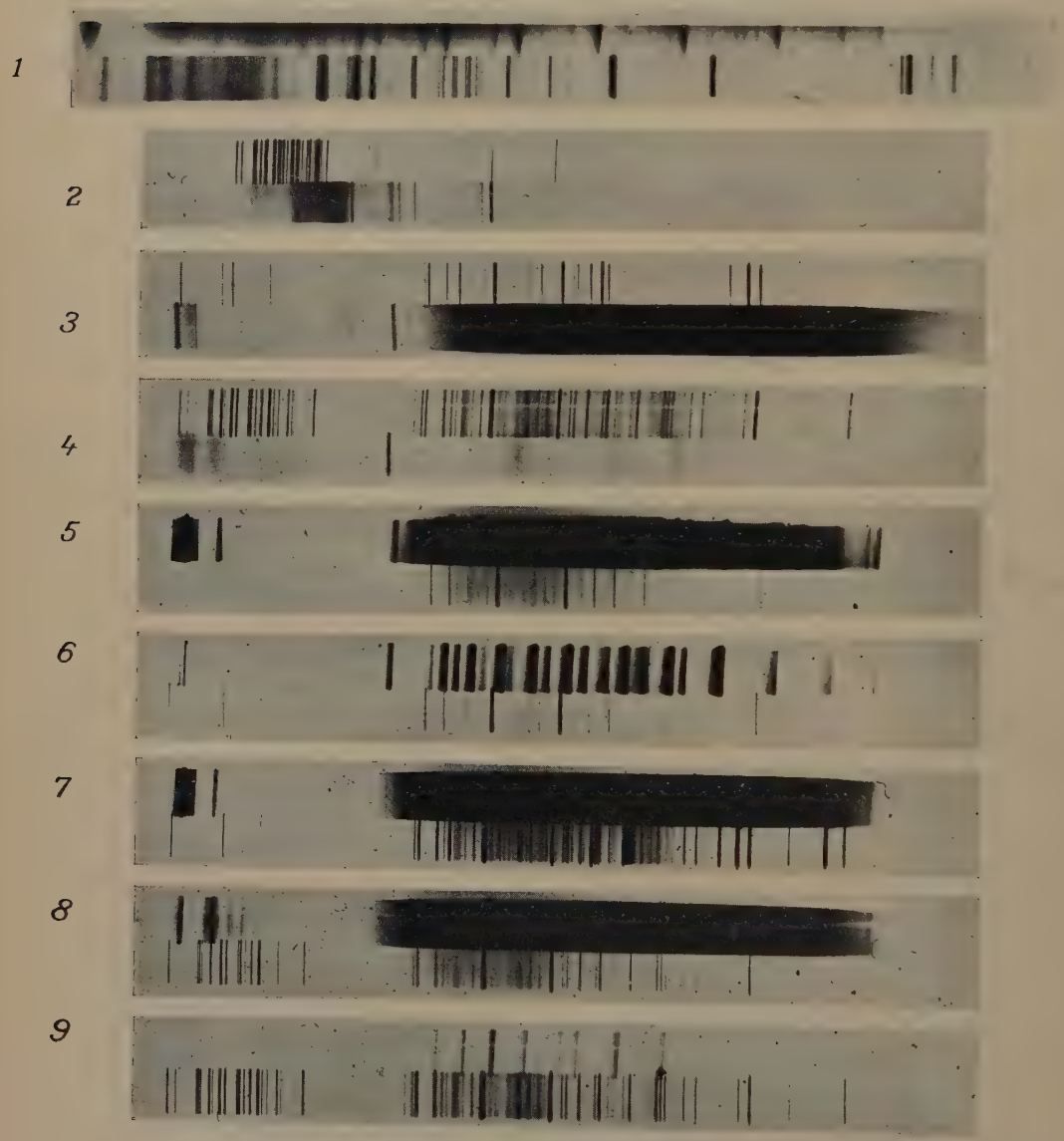
[1]) See e.g. L. VEGARD. Ann. d. Phys. **6**, 487, 1930 and Z. S. f. Phys. **75**, 30, 1932.

Now the state A is a metastable state, and in gaseous nitrogen we do not observe the ε-series corresponding to the transition from A to the normal molecular state because the metastable state is disturbed by collisions before emission occurs.



In α-nitrogen, however, the molecular elements are fixed in the space lattice, the metastable state is kept undisturbed for a sufficiently long time for the transition from A towards the normal state to take place, and the ε-system is emitted. In this way we explain the phosphorescence of the α-nitrogen as essentially depending on the existence of metastable states,

from which emission occurs, because in the α-form these states are not so easily disturbed.

In the β-form, however, the molecular elements rotate, and through this rotation the metastable states will be disturbed before the forbidden transition and the corresponding light emission can take place.

Explanations to the plate.

No. 1: Quartz spectrograph, Nos. 2—9: Large glass spectrograph.

No.	Solid system	Date	Tension of the tube	Time of exposure	Photographic plate	
			Volts	Hours		
1	"Pure" Kr.	12/2 —32	3500	$1^1/_2$	Barnet super speed ortho	Direct luminescence
2	„ „	3/3 —33	5000	4	Barnet pan plates	Direct luminescence
3	Pure N_2	22/4 —32	4000	$5^1/_2$	Agfa Infra rot 810 $\mu\mu$	Direct luminescence
4	„ „	28/10—32	4500	7	Agfa Infra rot 700-900$\mu\mu$	Afterglow
5	A + 3.5% N_2	10/2 —33	4000	2	Ilford Infra red pl.	Direct luminescence
6	A + 3.5% N_2	10/2 —33	4000	10	Ilford Infra red pl.	Afterglow
7	"Pure" A	26/2 —32	2700	3	Agfa Infra rot 810	Direct luminescence
8	„ „	9/12—32	4000	$1^1/_2$	Agfa Infra rot 700-900	Direct luminescence
9	„ „	9/12—32	4000	$3^1/_4$	Agfa Infra rot 700-900	Afterglow

The store of phosphorescence energy probably consists in a kind of molecular dissociation produced by the action of the electric rays, and through the recombination process the metastable states are excited. In the α-form this recombination process is very slow, in the β-form where the rays may also produce a dissociation the recombination process, owing to the molecular rotation, will occur almost instantaneously, and we get no store of phosphorescent energy and no phosphorescence. In this way structure analysis led to a simple explanation of the fact that solid nitrogen loses its phosphorescent power when it is transferred from the α- into the β-modification.

In connection with the structure analysis of α- and β-nitrogen, we have also taken up investigations on the structure of the various modifications of solid oxygen. We obtained powder diagrams of form I, which is stable between —229° C and the melting point, and form II, stable between —249

and —229° C. We have not yet been able to complete the structure analysis of these modifications, but there are certain facts which indicate that the molecular elements rotate in form I.

In conclusion I wish to express my sincere thanks to Mr. S. STENSHOLT and Mr. TH. RINGDAL for their most valuable assistance in connection with the investigations described in this paper.

Physical Institute, Oslo. March 1933.

Physics. — *The influence of time on the spreading of proteins.* By EVERT GORTER and G. TH. PHILIPPI. (Physical laboratory of the pediatric clinic of the University of Leiden). (Communicated by Prof. J. V. D. HOEVE).

(Communicated at the meeting of November 24, 1934).

The method for forming protein films on the surface of a *Langmuir* tray, used by us, consists in blowing out over the water surface a 0.5 % solution from a calibrated pipette containing 0.005 cc. The pipette is held in a horizontal position, so that the sharp point is above the water surface.

If the spreading of proteins is studied, results differ according to the *time* elapsing between the moment the micropipette, containing the protein solution is blown out at the surface and the beginning of the reading of the surface-area at different pressures.

Consistent results are easily obtained, if all measurements are made after a constant time, usually one or two minutes, calculated from the moment the pipette has been blown out until the beginning of the compression of the film.

When applying this technique (fig. 1) curves as have been published by us (1) are obtained.

Now it can be shown, that time has a very distinct influence on the results. Maximal spreading (the spreading number or spreading value is found by extrapolating the surface-pressure curve to zero pressure) is obtained within one or two minutes, if the conditions, which produce spreading, are optimal. On the other hand spreading over a smaller surface than the maximal one can often be shown to become maximal, if sufficient time is allowed. On the minima of the curve of ovalbumin (at pH = 2.5 and 6.5 in fig. 1) time again has a very slight influence.

The influence of time was studied separately by measuring surface potentials.

By this method the spreading process can be studied directly (2), the

presence of the protein on the surface giving rise to a very distinct change of the surface potential.

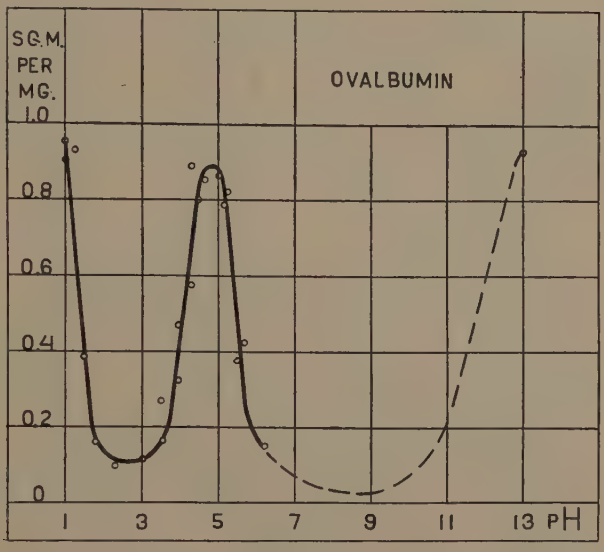


Fig. 1.

On the abscissa are plotted the pH values of the solutions on which the protein was spread, below pH 3.6 HCl-solutions, above pH 3.6 buffers 1/300 N were used. The dotted part of the curve has not yet been measured in detail. On the ordinates are plotted the area of the protein films, found by extrapolation surface-pressure curves to zero-pressure.

It was found that, just after the pipette has been blown out, the protein film is limited to a small circle around the pipette, the boundary *B* of which is wandering over the surface with a certain velocity (fig. 2), which

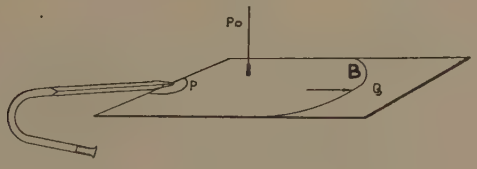


Fig. 2.

could be measured by following this boundary with the air-electrode Po (fig. 3).

It turned out that this time is a minimum at pH 1.0, at pH 13.0 and at the iso-electric point of the protein and is raised to high values on both sides of this point.

It will be clear at once, that when compression of the protein film is started before spreading is complete, the spreading number is smaller.

This is the explanation of the typical *W* curve, indicating the dependance of protein spreading on pH. In all the earlier experiments, when a longer

time was not specially indicated, compression was started one or two minutes after spreading. Therefore not in all cases the spreading process

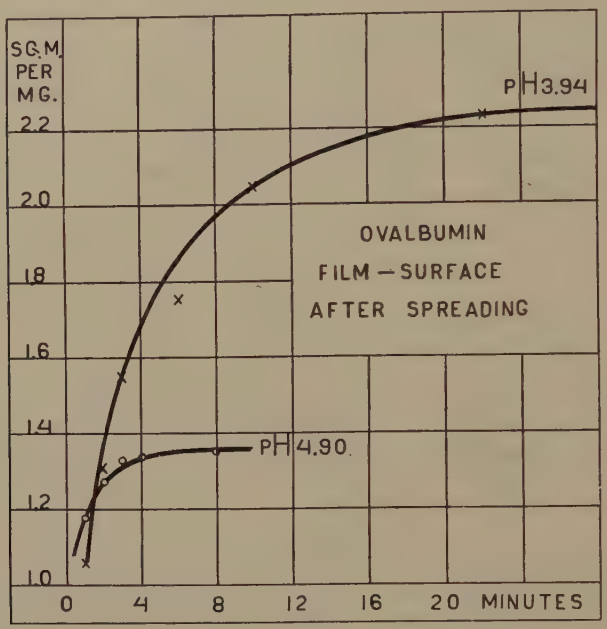


Fig. 3.

Here the protein was spread on acetate buffer 1/300 N. On the ordinates are plotted the areas of that part of the surface, as indicated in figure 2, that is covered by the protein film. These areas are measured with the movable Polonium electrode Po. The boundary B of the film is easily found, because there is a sharp difference in surface potential between the part of the surface which is covered by the film and that part which is not covered. On the abscissa are indicated the time values calculated from the moment the pipette has been blown out. The film at pH 4.90 is homogeneous as the variations of the surface-potentials are only 2—3 millivolt. The film at pH 3.94 is not homogeneous: here the variations amount to 20 millivolt.

came to an end. When one waits longer the tops of the W curve become more flat as can be seen from figure 4.

The time factor, the time in which equilibrium is reached, indicates a more or less stronger tendency to spread.[1])

Near the minima very long exposures are necessary to reach equilibrium in the case of ovalbumin. They are outside the experimental possibilities, because of the danger of the contamination of the surface. It is hardly possible to believe that in these cases even when measuring some hours after having brought the protein on the surface, true equilibria are formed.

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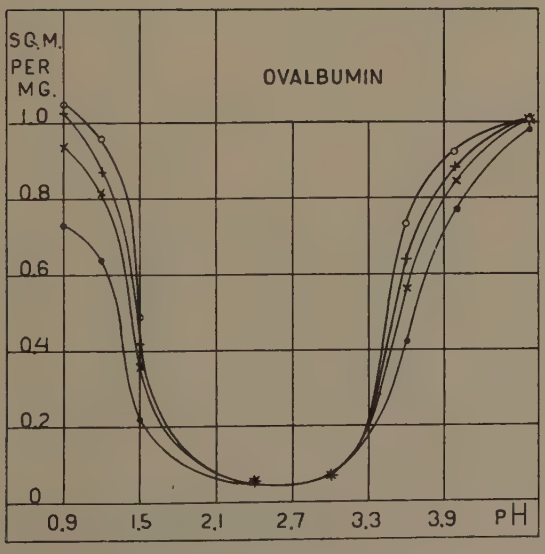
[1]) Compare E. GORTER en F. GRENDEL: De spreiding van oxy-haemoglobine. These Proceedings, **34**, 1925, 1257.

TABLE I.

PH of acetate buffer 1/300 *N*	Time required for boundary *B* to reach its final position
3.80	< 2 hours
3.94	< 1 hour
4.35	< 5′
4.61	< 3′
4.90	< 3′
5.05	< 10′
5.30	< 15′
5.72	< 9 hours
6.00	< 12 hours
PH of *HCl* solution	
1.07	< 10′
1.33	< 20′
1.62	< 30′
1.92	< 40′



Films compressed : Fig. 4.

. . . . 1 minute ++++ 8 minutes

XXXX 4 minutes o o o o 16 „

after the pipette containing the protein solution was blown out. Ordinates and abscissa as in figure 1 ; the same solutions were used.

If maxima are obtained by the addition of positive or negative ions at a pH, at which a maximal spreading in 1 or 2 minutes cannot be produced, the result is as rapidly obtained as in the case mentioned above, in which pH is the factor, that favours spreading.

Adding less of these ions gives intermediate values for the spreading area, which also tend to increase if time is allowed after the protein has been brought on the surface.

If one measures the potential differences over compressed proteinfilms at the point at which maximal spreading is seen on account of a suitable pH or ionic concentration, there are no larger variations observed between different spots of the surface than of 2—3 millivolt.

If, however, smaller areas than the maximal are studied by this method, inhomogenities are often found (2). This is in agreement with the results obtained by ZOCHER and STIEBEL (3), who have shown by ultramicroscopical investigation, that sometimes the films of proteins are not homogeneous.

It is therefore not permissible to calculate a thickness of the films near or at the minima of the curves. From the maximal spreading a thickness of 6—7.5 Å can be derived.

These minima occur when the protein has little spreading tendency and this can be due to either a too great solubility or to the reverse, a too small solubility. This is what occurs in the series of fatty acids, where the lower members are too soluble (up to C_{12}) for showing any spreading and the highest members (C_{60}) have too little spreading tendency owing to the fact, that they resemble too much a paraffin.

An example of a minimum due to small solubility is *myosin* (4); whereas *gelatin* exemplifies the minima due to a great solubility.

It is now easy to understand why the method used by LECOMTE DU NOUY (5) gives results which are comparable to ours if time is allowed in order to obtain equilibrium. From a solution the protein must move to the surface and it depends from the thickness of the waterlayer, the spreading tendency of the protein, and its diffusion coefficient how long this will take. The results obtained by WU (6) which differ from ours with regard to the time-factor only, are easily explained by a difference in technique. He makes use of dilute solutions of protein and of larger pipettes, so that a great part of the solution is blown under the surface and has to come out of it, which takes more time.

The method used by RIDEAL and HUGHES (7) who study protein crystals, which fall on the surface of the tray from a modified NERNST-balance gives results which are similar to ours.

Their numbers for *gliadin* at different pressure give a spreading of about one square meter per milligram, if the results are extrapolated to zero-pressure. This is the number we found for most proteins (8).

We are indebted to the ROCKEFELLER foundation for a grant by means of which these investigations have been made possible.

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Physics. — *On the electronic states of the N_2^+-molecule and their energies of dissociation.* By H. H. BRONS. (Communicated by Prof. D. COSTER.)

(Communicated at the meeting of November 24, 1934).

Introduction. Of the N_2^+-molecule four electronic states have been found. These are three $^2\Sigma$-states and one $^2\Pi$-state. The three $^2\Sigma$-states (see fig. 4) are known from transitions $b^2\Sigma \rightarrow a^2\Sigma$ and $c^2\Sigma \rightarrow a^2\Sigma$, the last transition recently having been found by WATSON and KOONTZ [1]).

The fourth electronic state $^2\Pi$ is only known from the perturbations it causes in the $b^2\Sigma$-state. Selection rules forbid transitions $c^2\Sigma \rightarrow {}^2\Pi$ and also $b^2\Sigma \rightarrow {}^2\Pi$. Transitions between the $^2\Pi$-state and the $a^2\Sigma$-state have not been found in the region of 2000 Å — 10000 Å, which might be understood if we assume these molecular states to lie at a very small distance from each other. Therefore all the knowledge about the $^2\Pi$-state has to be obtained from the perturbations it causes in the $b^2\Sigma$-state. Several of these perturbations have already been studied [2]). From these perturbations the values B_Π of the vibrational levels $v = X$, $v = X + 4$ and $v = X + 7$ (see fig. 2) are calculated in the following way [3]): The

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1) W. W. WATSON and P. G. KOONTZ, Phys. Rev. **46**, 32, 1934.

2) D. COSTER and H. H. BRONS, ZS. f. Phys. **73**, 747, 1932.
W. H. J. CHILDS, Proc. Roy. Soc. A **137**, 641, 1932.
ALLAN E. PARKER, Phys. Rev. **44**, 90, 1933 and **44**, 914, 1933.
H. H. BRONS, Physica **1**, 739, 1934.
H. H. BRONS, Dissertation Groningen 1934.

3) Compare: G. ITTMANN, ZS. f. Physik **77**, 616, 1931. D. COSTER and H. H. BRONS, ZS. f. Phys. **73**, 747, 1931. D. COSTER, H. H. BRONS and H. BULTHUIS, ZS. f. Phys. **79**, 787, 1932.

rotational-energy curves of the $b^2\Sigma$-state cross the rotational-energy curves of the perturbing $^2\Pi$-state. From the course of the perturbations one can determine at which value of J and hence at which value of the energy the crossing takes place. In calculating the B-values it is assumed that $B_{^2\Pi_{1/2}}$ and $B_{^2\Pi_{3/2}}$ are nearly the same; therefore in the following only the symbol B_Π is used. The energy of the rotational levels of both the $^2\Pi$-states can be represented as function of J by the following expressions:

$$^2\Pi_{3/2}\text{-state: } W = E + hcB_\Pi(J+\tfrac{1}{2})^2 \ldots . J = {}^3/_2, {}^5/_2 \quad . \quad . \quad . \quad (1)$$

$$^2\Pi_{1/2}\text{-state: } W = F + hcB_\Pi(J+\tfrac{1}{2})^2 \ldots . J = {}^1/_2, {}^3/_2 \quad . \quad . \quad . \quad (2)$$

For a determination of B_Π it is necessary to have at least two crossings of a definite $^2\Pi$-state with the $b^2\Sigma$-states. Here it must be remarked that the expressions (1) and (2) are only valid for J-values which are not too high. For high J-values, however, there must be added a term $hcD_\Pi\,(J+\frac{1}{2})^4$ on account of the increase of the moment of inertia with the value of J. We have also assumed that for both $^2\Pi$-states the D-values are the same. For the determination of B_Π and D_Π it is necessary to know a complete crossing of both $^2\Pi$ with both $b^2\Sigma$-states. In this case four unknowns (E, F, B_π and D_π) have to be determined, therefore we have to know four intersections. The B_Π-values found in this way are given in table 1.

TABLE 1.
B-values of the perturbing $^2\Pi$-state.

v	B_π
X	1.78
$X+4$	1.62
$X+7$	1.47

With the help of these B-values an estimate has been made of the position of the rotationless vibrational levels X, $X+4$ and $X+7$. These values are given in table 2. We have assumed as zero-point the rotationless level of the state $a^2\Sigma$ ($v=0$.). In fig 1 the relative positions of the perturbing

TABLE 2.
Position of the 0-rotationless levels of the $^2\Pi$-state.

v	$^2\Pi$
X	26356 cm^{-1}
$X+4$	32534 cm^{-1}
$X+7$	36841 cm^{-1}

$^2\Pi$- and $b^2\Sigma$-levels are given as they are estimated from the known perturbations.

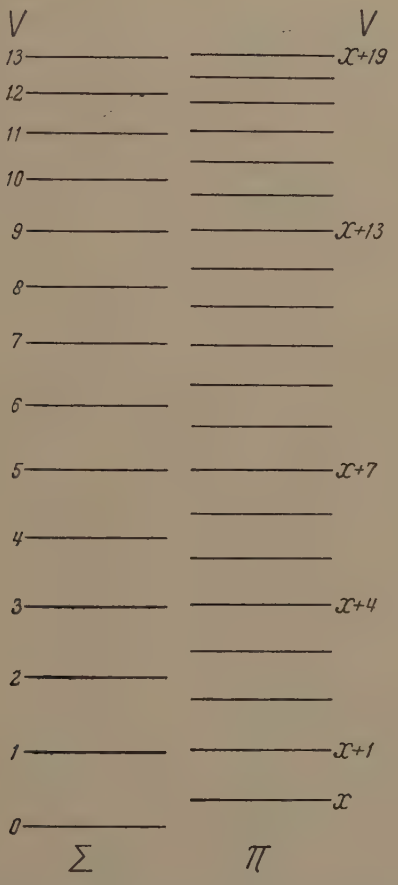

Fig. 1. Relative position of the vibrational $b^2\Sigma$-levels and the perturbing $^2\Pi$-levels in the N_2^+-molecule.

Energies of dissociation and potential-curves. The course of the *B*-values of the $b^2\Sigma$-state shows that this state dissociates at about $v' = 20$. Substituting this value into the vibration formula [4]), we get a value of the energy of dissociation of 3.12 *V*. From the vibration formula itself, however, according to BIRGE and SPONER [5]) it follows that dissociation takes place at $v_{max.} = 17$ and this gives as a value for the dissociation energy 3.27 *V*. Therefore it looks quite reasonable to assume for the value of the energy of dissociation of the $b^2\Sigma$-state 3.2 ± 0.1 *V*. The distance between the two electronic states $a^2\Sigma$ and $b^2\Sigma$ amounts to 3.15 *V*. If we assume that the state $b^2\Sigma$ dissociates into the lowest atomic states, we find for the energy of dissociation of the N_2^+-molecule the value $E = 3.15 + 3.2 = 6.3$ *V*. From this also the energy of dissociation of the

[4]) D. COSTER and H. H. BRONS, l.c.

[5]) R. T. BIRGE and H. SPONER, Phys. Rev. **28**, 259, 1926.

N_2-molecule can be calculated. According to HERZBERG [6]) we have:

$$I_m - I_a = D - E \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which I_m is the ionization potential of the normal nitrogen molecule, which is estimated to be 15.65 V. I_a is the ionization potential of the nitrogen atom, which we know exactly from the spectra of the atom. ($I_a = 14.49\ V$). We found for the dissociation energy of the N_2^+-molecule $E = 6.3\ V$. From this it follows from (3) that $D = 7.5\ V$. Recently KAPLAN [7]) found a new bandsystem of the normal N_2-molecule in the ultraviolet region. From this the value of D can be estimated with the help of the results of COSTER, BRONS and VAN DER ZIEL [8]) and is found to be $D = 7.33\ V$ [9]) with which the value found above is in good agreement. The energy of dissociation of the N_2-molecule is on the other hand also estimated by LOZIER [10]). Making use of the result of KAPLAN he finds the value $D = 7.4\ V$, also in good agreement with the above value.

For the $a^2\Sigma$-state we get according to BIRGE and SPONER for $v_{max.}$ the value 56 and this furnishes for the energy of dissociation of the state $a^2\Sigma$ the value 8.00 V. On account of the very long extrapolation we cannot give a high accuracy to this value. Probably it lies lower and in this case we have to assume that $a^2\Sigma$ dissociates into the same atomic states as the $b^2\Sigma$-state, which gives for its energy of dissociation 6.3 V.

Formerly HEITLER and HERZBERG [11]), assumed that the ground-state of the N_2^+-molecule should dissociate into an excited atom and a normal ion; MULLIKEN [12]), however, already has assumed that the products of dissociation should be a normal atom and a normal ion, which in view of the latest value of the energy of dissociation looks most probable.

Now for the different states we have drawn the potential curves with the help of the formula of MORSE [13]). For the derivation of this formula MORSE supposes that the vibrational energy of a diatomic molecule (oscillator) can be represented by a quadratic formula:

$$E(v) = h\omega_0 \{(v + \tfrac{1}{2}) - x(v + \tfrac{1}{2})^2\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which ω_0 is the natural frequency for small amplitudes and x is a measure for the anharmonicity of the oscillator.

From the expression (4) MORSE has derived on the basis of quantum mechanics a formula for the potential energy of the molecule as a function of the distance of the nuclei which has the following form:

$$E_r = D\, e^{-2a(r-r_0)} - 2D\, e^{-a(r-r_0)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

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[6]) G. HERZBERG, Nature **122**, 505, 1928.
[7]) J. KAPLAN, Phys. Rev. **44**, 947, 1933.
[8]) D. COSTER, F. BRONS and A. VAN DER ZIEL, ZS. f. Phys. **84**, 304, 1933.
[9]) G. HERZBERG and H. SPONER, ZS. f. phys. Chem. (B) **26**, 1, 1934.
[10]) W. W. LOZIER, Phys. Rev. **45**, 840, 1934.
[11]) W. HEITLER and G. HERZBERG, ZS. f. Phys. **53**, 52, 1929.
[12]) R. S. MULLIKEN, Rev. of Mod. Phys. **4**, 1, 1932.
[13]) P. M. MORSE, Phys. Rev. **34**, 57, 1929.

D is the energy of dissociation; r_0 the distance of the nuclei in the position of equilibrium. Furthermore $a = \sqrt{\frac{8\pi^2 c\,\mu\,\omega_0}{h}}$ in which μ denotes the reduced mass. If we know ω_0, x and besides D, we can get with the help of (5) a good representation of the potential curves. For the states $a^2\Sigma$ and $b^2\Sigma$ we did not take the energies of dissociation, which should follow from a quadratic formula as (4) because for these states very accurate dissociation energies are already known. All the other constants in the formula of MORSE are also calculated from experimental data. For $a^2\Sigma$ we get:

$$D = 6.3\ V;\ a = 2.65 \text{ and } r_0 = 1.12\ \text{Å},$$

for $b^2\Sigma$:

$$D = 3.2\ V;\ a = 3.22 \text{ and } r_0 = 1.08\ \text{Å}.$$

Thus we obtain approximate potential curves for these two states (Fig. 2).

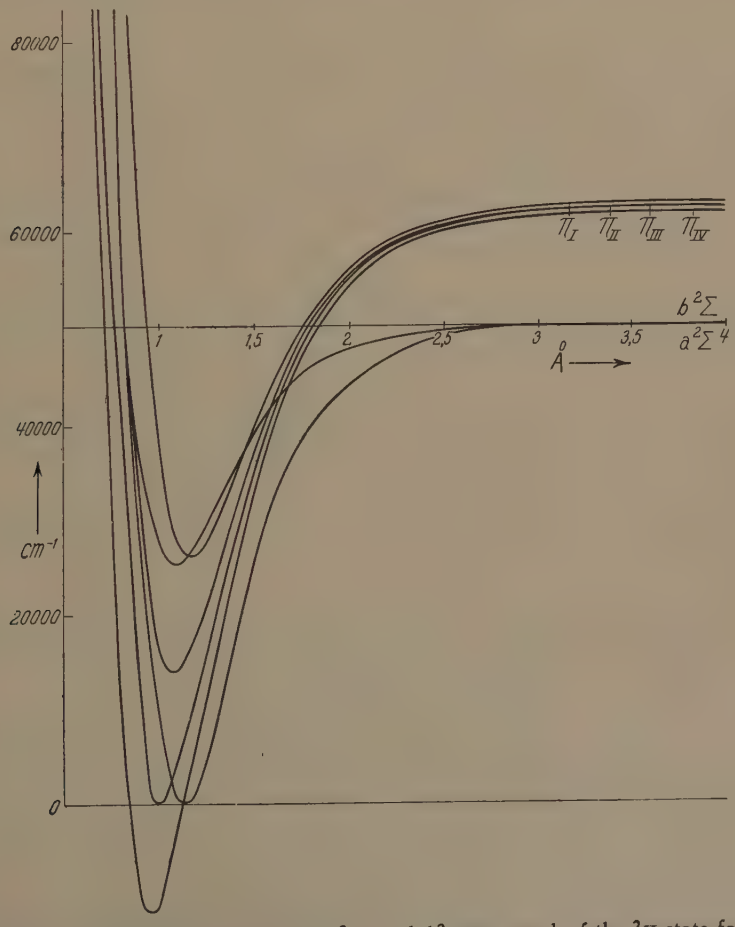

Fig. 2. Potential curves of the $a^2\Sigma$- and $b^2\Sigma$-state and of the $^2\Pi$-state for four different values of X namely $X = 0$, $X = 7$, $X = 15$ and $X = 20$.

For the perturbing $^2\Pi$-state the difficulty arises that we do not know the value of X (see fig. 1). Hence we have assumed for X different values and we have drawn the potential curves for these different cases. The constants which we have to use in the four cases are given in table 3. All these constants are derived only from the constants of the three levels X, $X+4$ and $X+7$ (see fig. 1) and thus it is easily understood that the values of table 3 only are rough approximations. For the four cases of

TABLE 3.

Case	X	B_0 in cm^{-1}	r_0 in Å	H*) in cm^{-1}	D in V	v
I	0	1.78	1.16	+ 26366	4.6	2.76
II	7	2.07	1.07	+ 16043	6.1	2.76
III	15	2.46	0.99	— 34	7.8	2.76
IV	20	2.68	0.95	— 11169	9.1	2.76

*) This column gives the position of the level $^2\pi$ $v=0$ with regard to the level $a^2\Sigma$ $v=0$ which is taken as zero-point.

table 3 the potential curves are constructed according to MORSE. They are also given in figure 2. It seems to us most probable that the real potential curve for the $^2\Pi$-state lies between the cases II and III. From the considerations given above about the energy of dissociation in connection with the cyclical process of HERZBERG, it follows that the 0-vibration of the $^2\Pi$-state lies above that of the $a^2\Sigma$-state. This is also in agreement with what has been found for the molecules BO, CN and CO^+ with equal number of electrons. On the other hand it will be clear that the distance between the 0-vibration of $^2\Pi$ and $a^2\Sigma$ cannot be very large either since the transitions $^2\Pi \rightarrow a^2\Sigma$ have never been found in the emissionspectrum [14]). From these considerations we may even limit a little more narrowly the value of X:

$$10 \leqq X \leqq 15.$$

As regards the energy of dissociation of the $^2\Pi$-state for the different cases, it must be remarked, that in consequence of the method which has been followed, in all probability too high values have been found. From fig. 2 we have to conclude, that the products of dissociation of the $^2\Pi$-state should have 1.5 V more energy than those from the $a^2\Sigma$ and $b^2\Sigma$-states. The lowest possible excited energy of the products of dissociation (N in the state ^2D, N^+ normal), however, lies 2.4 V above the ground state. It therefore looks much more reasonable to assume, that also the $^2\Pi$-state dissociates into the ground states of N^+ and N.

[14]) I have also looked for this spectrum in vain in the whole region of 2000—10000 Å.

Starting from this assumption we have drawn fig. 3. As regards this figure the following remarks may be made: The potential curves for both $^2\Sigma$-states have simply been taken from fig. 2. The curve for $^2\Pi$ is drawn as it appeared to be most probable. Here still the following considerations have been taken into account:

In the case of perturbations the rule holds, that they are only of noticeable size if in the neighbourhood of the energy value of the perturbing levels a point of intersection of the potential curves of the electronic states is lying i.e. if the distance of the nuclei in such a case does not differ too much for the two electronic states considered. Now it is found that

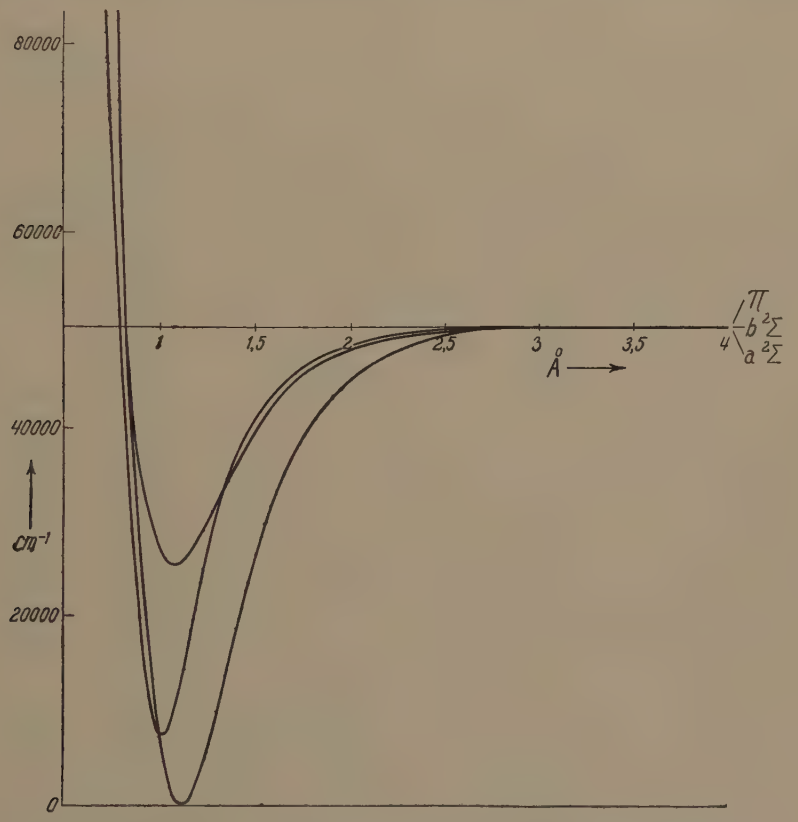

Fig. 3. Potential curves of the electronic states of the N_2^+-molecule as they seem us most probably to be.

perturbations appear in $b^2\Sigma$, $v'=0$, 1, 2, 3, 5, 9 and 13, where it must be remembered that $v'=13$ lies already near the limit of dissociation. Furthermore we have to remark that the perturbation in the level $v'=3$ is the greatest. Towards lower and higher v-values, the size of the perturbations decreases. Therefore we may assume that in the neighbourhood of $v'=3$ the potential curves of $b^2\Sigma$ and $^2\Pi$ have to intersect. From the limits for X obtained above, however, it follows that for the $^2\Pi$-state the distance

of the nuclei in the position of equilibrium is much smaller than for the $b^2\Sigma$-state. The most probable value is about 1.02 Å, and this excludes the possibility of an intersection of the potential curves on the left side of the figure. Thus the intersection lies on the right side and from this it follows that the right hand sides of the potential curves of $b^2\Sigma$ and $^2\Pi$ are rather close to each other. This affords at the same time another reason for assuming the states $b^2\Sigma$ and $^2\Pi$ to dissociate into the same atomic states.

From the course of the potential curves we even can narrow a little more the limits for the value of X, namely: $11 \leqq X \leqq 13$. In this way we come to a fairly well established course of the $^2\Pi$-potential curve. Here we must remark once more, that the position of the $^2\Pi$-state is not estimated from transitions with other electronic states, but only by the perturbations it causes in the $b^2\Sigma$-state.

Products of dissociation. The terms of the normal nitrogen atom as well as those of the ionized nitrogen atom are measured and classified [15]). For the estimation of the possible atomic states into which the ionized nitrogen molecule can dissociate only the lowest terms with the electronic configurations for N, $(1s)^2\ (2s)^2\ (2p)^3$ and for N^+ with $(1s)^2\ (2s)^2\ (2p)^2$ come

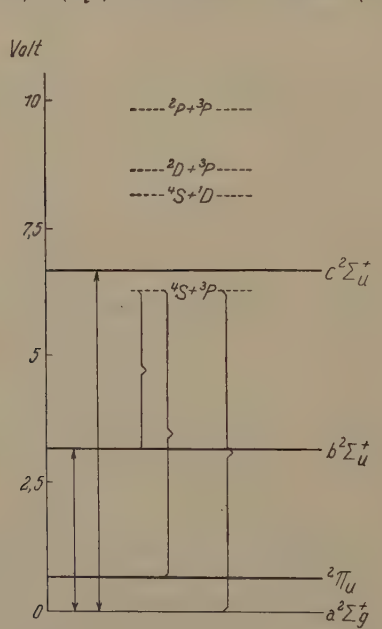

Fig. 4. Scheme of the electronic states of the N_2^+-molecule, with the atomic states in which they are dissociating. The fully drawn lines are the known energy niveaus, the dotted lines the known terms of dissociation. The vertical arrows give the observed transitions; the brackets combine the electronic levels with the atomic states into which they dissociate.

[15]) K. T. COMPTON and J. C. BOYCE, Phys. Rev. **33**, 145, 1929.
S. B. INGRAM, Phys. Rev. **34**, 145, 1929.
E. EKEFORS, ZS. f. Phys. **63**, 437, 1930.

into consideration. According to the Pauli-principle these are the terms ^4S, ^2D and ^2P of the normal atom and the terms ^3P, ^1D and ^1S of the ionized atom. This gives the following different terms of dissociation written down in the order of increasing energy: $(^4S + {}^3P)$, $(^4S + {}^1D)$, $(^2D + {}^3P)$, $(^2P + {}^3P)$, $(^4S + {}^1S)$, $(^2D + {}^1D)$, $(^2P + {}^1D)$, $(^2D + {}^1S)$ and $(^2P + {}^1S)$.

The three states $a^2\Sigma$, $b^2\Sigma$ and $^2\Pi$ all dissociate into the same term $(^4S + {}^3P)$; of the other known state $c^2\Sigma$ we still do not know the terms of dissociation. Fig. 4 gives the level scheme of the electronic levels, known up to now, of the N_2^+-molecule. Since of the $^2\Pi$-state we only know the lower and upper limit of this position, we have drawn this state half way between these limits, which gives an uncertainty < 0.5 V.

Symmetry of the electronic states. The $a^2\Sigma$-, $b^2\Sigma$- and $^2\Pi$-states thus dissociate into the atomic terms $(^4S + {}^3P)$. With the help of the rules of HUND [16]) and WIGNER and WITMER [17]) it follows that from these atomic terms for the $a^2\Sigma$- and $b^2\Sigma$-state we have the possibilities $^2\Sigma_u^+$ and $^2\Sigma_g^+$. Now the lines of the N_2^+-bands show intensity alternation (2) in consequence the presence of a nuclear spin. The nitrogen nucleus follows the statistics of BOSE-EINSTEIN [18]). In this case the factors of weight for symmetrical and antisymmetrical states have the ratio $\frac{gs}{ga} = \frac{I+1}{I}$. As we know this ratio to be 2 for the N_2^+ band lines, we may conclude the nuclear spin to be 1 [19]). As the lines with even K are the most intense [20]), we may conclude that of the state $a^2\Sigma$ the even levels are symmetrical and this gives for the symmetry of $a^2\Sigma$ only the possibilities $^2\Sigma_g^+$ and $^2\Sigma_u^-$. We thus find that the state $a^2\Sigma$ must be a $^2\Sigma_g^+$-state. From this we can derive at once the symmetry of the other states on the basis of the existence of transitions and perturbations. We then find for the four known electronic states of the N_2^+-molecule successively: $a^2\Sigma_g^+$, $^2\Pi_u$, $b^2\Sigma_u^+$ and $c^2\Sigma_u^+$.

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16) F. HUND, ZS. f. Phys. **63**, 719, 1930.

17) E. WIGNER and E. E. WITMER, ZS. f. Phys. **51**, 859, 1928.

18) F. RASETTI, Proc. Nat. Acad. Amer. **15**, 515, 1929, ZS. f. Phys. **61**, 598, 1931. W. HEITLER and G. HERZBERG, Naturwissenschaften **17**, 673, 1929.

19) L. S. ORNSTEIN and W. R. VAN WIJK, ZS. f. Phys. **49**, 315, 1928.

20) This is clearly seen on the photometer curve of the (8.6) band. (See D. COSTER and H. H. BRONS, ZS. f. Phys. **73**, pag. 765, 1932.

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Mathematics. — *A geometric interpretation of a Theorem on skew symmetric functions.* By R. RAMAMURTI. (Communicated by Prof. R. WEITZENBÖCK).

(Communicated at the meeting of November 24, 1934).

In a paper on skew symmetric functions Dr. WEITZENBÖCK[1]) has obtained a necessary and sufficient condition that a skew symmetric function $K(s, t)$ of two complex variables s and t should be of rank r (i.e.) that an identity exists of the form

$$K(s, t) = \sum_{k=1}^{r} \{\varphi_k(s)\,\psi_k(t) - \varphi_k(t)\,\psi_k(s)\}$$

and r is the smallest number for which such an identity exists. Consider the Pfaffian Aggregates

$$P_1(s_1, s_2) = K(s_1, s_2)$$

$$P_2(s_1, s_2, s_3, s_4) = K(s_1, s_2)\,P_1(s_3, s_4) - K(s_1, s_3)\,P_1(s_2, s_4) + K(s_1, s_4)\,P_1(s_2, s_3)$$

$$P_\rho(s, s_2, \ldots, s_{2\varphi}) = K(s_1, s_2)\,P_{\rho-1}(s_3, s_4, \ldots, s_{2\rho}) - K(s_1, s_3)\,P_{\rho-1}(s_2, \ldots, s_{2\rho})$$
$$\ldots + (K s_1, s_{2\rho})(s_2 s_3, \ldots, s_{2\rho-1}).$$

Then Dr. WEITZENBÖCK's theorem says:

A necessary and sufficient condition that $K(s_1, s_2)$ should be of rank r is that

$$P_r \not\equiv 0 \text{ and } P_{r+1} \equiv 0 \quad \ldots\ldots\ldots \quad (1)$$

The object of this note is to give a geometric interpretation of the above investigation, when $K(s, t)$ is a skew symmetric algebraic form of degree n in s and in t and to supply a geometric proof of the result.

Let us take a rational norm curve R_n in a projective space S_n of n dimensions, given parametrically by

$$x_r = s^r \qquad (r = 0, 1, \ldots, n) \quad \ldots\ldots\ldots \quad (2)$$

and a linear line-complex L whose equation in line-coordinates is

$$\pi_a^2 = \sum_{0,n} a_{ik}\,\pi_{ik} = 0 \quad \ldots\ldots\ldots \quad (3)$$

[1]) Rendiconti di Palermo, 33 (1912), p. 1—10.

The nullsystem N defined by L is given by

$$\sum_{0,n} a_{ik}(x_i y_k - x_k y_i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The points s, and t on R_n are conjugate with respect to N (i.e. the chord joining the two points belongs to the linear complex L) if

$$K(s,t) = \sum_{0,n} a_{ik}(s^i t^k - s^k t^i) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

so that $K(s,t)$ is a skew symmetric algebraic form of degree n in s and in t. Conversely given any skew symmetric form $K(s,t)$, there is a unique nullsystem N (and the associated linear complex L) with respect to which the points s, and t on R_n are conjugate if $K(s,t)$ [1]$= 0$.

Theorem I. *The Pfaffian $P_r(s_1, s_2, \ldots, s_{2r})$ of $K(s,t)$, equated to zero, gives the condition that the chordal (Sekanten) space S_{2r-1} of R determined by the points $s_1, s_2, \ldots, s_{2r}$ of R_n should cut the linear complex L in a nullvariant complex.* [2])

Proof. Obviously $P_1 = 0$ gives the chords of R_n which belong to L. Let us consider $P_2 = 0$. The S_3 determined by the points A_1, A_2, A_3, A_4 on R_n with the parameters s_1, s_2, s_3, s_4 respectively cuts L in a linear complex, whose equation in line coordinates is

$$\sum_{1,4} w_{ik}\, a_{A_i} a_{A_k} = 0$$

This is nullvariant [3]) if

$$\begin{vmatrix} a_{A_1} & a_{A_2} & a_{A_3} & a_{A_4} \\ a_{A_1} & a_{A_2} & a_{A_3} & a_{A_4} \\ b_{A_1} & b_{A_2} & b_{A_3} & b_{A_4} \\ b_{A_1} & b_{A_2} & b_{A_3} & b_{A_4} \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where a and b are equivalent complex-symbols.

From (4)

$$K(s_1, s_2) = \sum_{0,1} a_{ik}(s_1^i s_2^k - s_2^i s_1^k) = a_{A_1} a_{A_2} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

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[1]) WAELSCH, Über binäre Formen und die Correlationen mehrdimensionaler Räume. Monatshefte für Math. und Physik, Bd. 6.

[2]) A linear complex $\pi_a^2 = 0$ in S_{2n-1} is said to be null-variant by Dr. WEITZENBÖCK if its invariant $J = (a^2\, b^2 \ldots |n| \ldots m^2)^2 = 0$.

Geometrically it may be characterised as one containing one and hence at least ∞^1 singular points. To keep up analogy with the tangential regions of a quadric, they may also be called tangential regions of a linear complex, in as much as, they are regions self-conjugate with respect to the nullsystem defined by the linear complex.

[3]) C.f. WEITZENBÖCK, Komplex-Symbolik p. 166.

Hence expanding (6) and using (7) we have

$$\left.\begin{aligned} K(s_1, s_2)\,K(s_3, s_4) - K(s_1, s_3)\,K(s_2, s_4) + K(s_1, s_4)\,K(s_2, s_3) &= 0 \\ \text{(i.e.)} \qquad P_2(s_1, s_2, s_3, s_4) &= 0 \end{aligned}\right\} \quad (8)$$

Similarly, the chordal S_5 joining the points $s_1, s_2, \ldots . s_6$ on R_n cuts L in a nullvariant complex if the determinant

$$(a_{A_1}\, a_{A_2}\, b_{A_3}\, b_A\ \ c_{A_5}\, c_{A_6}) = 0 \quad . \ . \ . \ . \ . \ . \quad (9)$$

On expanding (9) and using (8), (9) becomes

$$K(s_1, s_2)\,P_2(s_3, s_4, s_5, s_6) - K(s_1, s_3)\,P_2(s_2, s_4, s_5, s_6) + \ldots . + K(s_1, s_6)\,P_2(s_2, s_3, s_4, s_5) = 0$$

$$\text{(i.e.)} \qquad P_3(s_1, s_2, s_3, s_4, s_5, s_6) = 0$$

Similarly, it can be shown by Induction that the chordal S_{2r-1} determined by the points $s_1, s_2 \ldots . s_{2r}$ on R_n cuts L in a nullvariant complex if $P_r(s_1, s_2, \ldots . s_{2r}) = 0$. Thus Theorem I is proved.

The linear complex L_k determining on R_n the correspondence of points given by

$$\varphi_k(s)\,\psi_k(t) - \varphi_k(t)\,\psi_k(s) = 0 \quad . \ . \ . \ . \ . \ . \quad (10)$$

is a special linear complex consisting of all the lines intersecting the S_{n-2} common to the two S_{n-1}'s cutting out on R_n the point-sets given parametrically by $\varphi_k(s) = 0$ and $\Psi_k(s) = 0$.

L_k is of rank 2[1]). If $K(s, t)$ is of rank r, it can be expressed as the sum of at least r forms of the type (10). Henze L can be expressed as a sum of at least r special complexes. Then L is of rank $2r$. Conversely if L is of rank $2r$, $K(s, t)$ is of rank r. Hence the geometric interpretation of Dr. WEITZENBÖCK's theorem is:

A necessary and sufficient condition that a linear complex L in S_n should be of rank $2r$ is that every chordal (sekanten) S_{2r+1} of the rational norm curve R_n should cut L in a nullvariant complex, and that this property should not be true for every chordal S_{2r-1}.

To prove the theorem geometrically, we require the following Lemmas.

Lemma 1. There can be no S_{n-r-1} intersecting all the osculating S_rs of a rational norm curve R_n.

Lemma 2. If every osculating S_{2r+1} of R_n cuts L in a nullvariant complex, the linear complex cannot be of rank $2r+2$.

To prove Lemma 1, we take any S_{n-r-1}. The ∞^r primes through it, cut out on R_n sets of points given parametrically by a linear ∞^r system of binary n-ics. The Jacobian of the system which is of order $(r+1)(n-r)$

[1]) The rank of the linear complex $\sum_{0,n} a_{ik}\ \pi_{ik} = 0$ is the rank of the matrix $\| a_{ik} \|$.

gives the roots of the above system of n-ics, which are of multiplicity $(r+1)$. If α is a root of the Jacobian, the osculating S_r at the point α of R_n must meet the S_{n-r-1} and conversely. Hence there are only $(r+1)(n-r)$ osculating S_rs of R_n meeting any S_{n-r-1} unless the Jacobian vanishes identically which is impossible, since the n-ics form a linear ∞^r system.

To prove Lemma 2, let us suppose L is of rank $2r+2$. Then the singular points of L form a S_{n-2r-2}. Then it is known that any S_{2r+1} not intersecting the S_{n-2r-2} must cut L in a nonsingular complex. But form Lemma 1, we can always find an osculating S_{2r+1} not intersecting S_{n-2r-2}, and from the hypothesis of Lemma 2, this cuts L in a nullvariant complex which is contradictory to the above statement. Hence L cannot be of rank $(2r+2)$.

Coming now to the theorem proper, suppose every chordal $S_{(2r+1)}$ cuts L in a nullvariant complex. Then $P_{r+1} \equiv 0$ and hence $P_{(r+1+\lambda)} \equiv 0$ $(\lambda \gtrless 0)$. Hence every chordal $S_{2r+2\lambda+1}$ and in particular every osculating $S_{(2r+2\lambda+1)}$ cuts L in a nullvariant complex. Therefore from Lemma 2, L cannot be of rank $(2r+2+2\lambda)$. Also it cannot be of rank $< 2r$, for if it is $(2r-2\lambda)$, every $S_{(2r-2\lambda+1)}$ and in particular, every osculating $S_{(2r-2\lambda+1)}$ must cut L in a nullvariant complex. Then $P_{(2r-2\lambda+2)} \equiv 0$ and hence $P_{2r} \equiv 0$, which is against hypothesis. Therefore L must be of rank $2r$. Thus the conditions $P_{r+1} \equiv 0$ and $P_r \not\equiv 0$ are sufficient.

To prove that they are necessary, suppose L is of $2r$. Then it has a S_{n-2r} of singular points. Hence any chordal S_{2r+1} will cut the singular region in a straight line and hence will cut L in a nullvariant complex. Therefore $P_{r+1} \equiv 0$. Also $P_r \not\equiv 0$ for if $P_r \equiv 0$, from Lemma 2, L cannot be of rank $2r$.

Mathematics. — *Einige Integraldarstellungen für* WHITTAKER*sche und* BESSEL*sche Funktionen.* Von C. S. MEIJER. (Communicated by Prof. J. G. VAN DER CORPUT).

(Communicated at the meeting of November 24, 1934).

§ 1. Integraldarstellungen für die WHITTAKERsche Funktion.

Bekanntlich besitzt die parabolische Zylinderfunktion $D_n(z)$, falls $\Re(n) < 0$ ist, die folgende Integraldarstellung [1])

$$D_n(z) = \frac{e^{-\frac{1}{4}z^2}}{\Gamma(-n)} \int_0^\infty e^{-zt-\frac{1}{2}t^2}\, t^{-n-1}\, dt \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1]) Man vergl.: E. T. WHITTAKER and G. N. WATSON, Modern Analysis, § 16.6 und § 12.22; C. S. MEIJER, Über die Integraldarstellungen der WHITTAKERschen Funktion $W_{k,m}(z)$ und der HANKELschen und BESSELschen Funktionen, Nieuw Archief voor Wiskunde (2e reeks) 18 (1934), S. 35—57, § 3. Diese beiden Arbeiten werden im folgenden immer mit M. A. und I zitiert.

Nun hat man [2])

$$D_n(z) = 2^{\frac{1}{2}n+\frac{1}{4}}\ z^{-\frac{1}{2}}\ W_{\frac{1}{2}n+\frac{1}{4},-\frac{1}{4}}(\tfrac{1}{2}z^2), \quad \ldots\ldots \quad (2)$$

wo $W_{k,m}(z)$ die WHITTAKERsche Funktion bezeichnet.

Es liegt jetzt nahe zu fragen, ob es eine Integralformel für $W_{k,m}(z)$ gibt, die Beziehung (1) als Spezialfall enthält, d. h. ob die Funktion $2^k z^{-\frac{1}{2}} W_{k,m}(\frac{1}{2}z^2)$ eine Integraldarstellung besitzt, die für $k=\frac{1}{2}n+\frac{1}{4}$, $m=-\frac{1}{4}$ gleich der rechten Seite von (1) wird. Die Antwort lautet folgendermaszen:

Ist $\Re(\frac{1}{2}\pm m-k)>0$, *so gilt für alle Werte von* $\arg\zeta$ [3])

$$W_{k,m}(\zeta^2) = \frac{4\zeta e^{-\frac{1}{2}\zeta^2}}{\Gamma(\frac{1}{2}+m-k)\,\Gamma(\frac{1}{2}-m-k)}\int_0^\infty e^{-u^2} K_{2m}(2\zeta u)\,u^{-2k}\,du\,. \quad (3)$$

Hierin ist

$$K_\nu(w) = \tfrac{1}{2}\pi i e^{\frac{1}{2}\nu\pi i} H_\nu^{(1)}(we^{\frac{1}{2}\pi i}) \quad \ldots\ldots \quad (4)$$

($H_\nu^{(1)}(w)$ ist die erste HANKELsche Funktion).

Es ist leicht einzusehen, dasz (1) ein Spezialfall von (3) ist. Denn es gilt [4])

$$K_{-\frac{1}{2}}(w) = \sqrt{\frac{\pi}{2w}}\,e^{-w}.$$

Setzt man nun $k=\frac{1}{2}n+\frac{1}{4}$, $m=-\frac{1}{4}$, $u=\dfrac{t}{\sqrt{2}}$ und $\zeta=\dfrac{z}{\sqrt{2}}$, dann geht also (3) mit Hilfe von (2) in (1) über [5]).

In der vorliegenden Abhandlung werde ich nicht nur (3) beweisen, sondern eine viel allgemeinere Integraldarstellung für $W_{k,m}(\zeta^2)$ ableiten, die (3) als Spezialfall enthält.

Ich setze [6])

$$\Phi(k;m,a,w) = \left.\begin{aligned} &= \frac{\Gamma(-2m)\,w^{m+\frac{1}{2}}}{\Gamma(\frac{1}{2}-m-k)\,\Gamma(\frac{1}{2}+m+a)}\ {}_1F_2(\tfrac{1}{2}+m-k;\,1+2m,\,\tfrac{1}{2}+m+a;\,w) \\ &+ \frac{\Gamma(2m)\,w^{-m+\frac{1}{2}}}{\Gamma(\frac{1}{2}+m-k)\,\Gamma(\frac{1}{2}-m+a)}\ {}_1F_2(\tfrac{1}{2}-m-k;\,1-2m,\,\tfrac{1}{2}-m+a;\,w) \end{aligned}\right\}. \quad (5)$$

---

[2]) Siehe M. A., § 16.5 und I, S. 54. Die Funktion $D_n(z)$ wird gewöhnlich durch (2) definiert.

[3]) Ich nehme an, dasz $\zeta\neq 0$ ist.

Die früher für $W_{k,m}(z)$ abgeleiteten Integraldarstellungen gelten nur für $|\arg z|<\dfrac{3\pi}{2}$; siehe M. A., Chapter 16 und I, S. 35—37.

$\Re(\frac{1}{2}\pm m-k)>0$ bedeutet $\Re(\frac{1}{2}+m-k)>0$ und $\Re(\frac{1}{2}-m-k)>0$.

[4]) Man vergl.: G. N. WATSON, A Treatise on the Theory of BESSEL Functions, S. 80, Formel (13). Dieses WATSONsche Werk wird in der Folge mit B. F. zitiert.

$K_\nu(z)$ ist eine gerade Funktion von ν.

[5]) $\Gamma(\tau)\,\Gamma(\tau+\frac{1}{2}) = 2^{1-2\tau}\sqrt{\pi}\,\Gamma(2\tau)$.

[6]) ${}_pF_q(a_1,\ldots,a_p;\,b_1,\ldots,b_q;\,w)$ ist eine verallgemeinerte hypergeometrische Funktion.

Hierin wird $2m$ nicht ganz und $\frac{1}{2} \pm m + \alpha \neq 0, -1, -2, \ldots$ vorausgesetzt.

Mein Ergebnis lautet nun folgendermaszen:

Ist $2m$ nicht ganz, so gilt für alle Werte von $\arg \zeta$

$$W_{k,m}(\zeta^2) = 2 e^{-\frac{1}{2}\zeta^2} \int_0^\infty e^{-u^2} \Phi(k, m, \alpha, \zeta^2 u^2)\, u^{2\alpha-1}\, du; \quad \ldots \quad (6)$$

Hierin ist α eine beliebige Zahl mit $\Re(\frac{1}{2} \pm m + \alpha) > 0$.

Es ist nicht schwer zu zeigen, dasz (3) ein Spezialfall von (6) ist. Denn man hat, falls ν nicht ganz ist[7]),

$$2K_\nu(2z) = \Gamma(-\nu)\, z^\nu\, {}_0F_1(1+\nu; z^2) + \Gamma(\nu)\, z^{-\nu}\, {}_0F_1(1-\nu; z^2).$$

Hieraus und aus (5) folgt[8])

$$\Phi(k, m, -k, z^2) = \frac{2z\, K_{2m}(2z)}{\Gamma(\frac{1}{2}+m-k)\,\Gamma(\frac{1}{2}-m-k)}.$$

Formel (3) ist also der Spezialfall mit $\alpha = -k$ von (6)[9]).

§ 2. Beweis von (6).

Sind b und $c \neq 0, -1, -2, \ldots$, so gibt es eine von a, b und c abhängige, positive Zahl λ mit der Eigenschaft

$$\left| \frac{(a+n)(1+n)}{(b+n)(c+n)} \right| < \lambda^2 \qquad (n = 0, 1, 2, \ldots).$$

Für beliebige komplexe Werte von w gilt also

$$|\,{}_1F_2(a; b, c; w^2)\,| \leqq 1 + \frac{(\lambda|w|)^2}{(1!)^2} + \frac{(\lambda|w|)^4}{(2!)^2} + \ldots.$$

$$\leqq \left(1 + \frac{\lambda|w|}{1!} + \frac{(\lambda|w|)^2}{2!} + \ldots.\right)^2,$$

somit

$$|\,{}_1F_2(a; b, c; w^2)\,| \leqq e^{2\lambda|w|}. \quad \ldots \quad (7)$$

Die rechte Seite von (6) ist daher wegen (5) für alle Werte von $\arg \zeta$ eine analytische Funktion von ζ.

---

7) Siehe B. F., S. 77, Formel (2) und S. 78, Formel (6).

8) Man sieht leicht ein, dasz

$${}_1F_2(a; b, a; w) = {}_0F_1(b; w)$$

ist.

9) Relation (3) ist noch nicht bewiesen worden, falls $2m$ ganz ist. Da aber (3) gilt für alle andere Werte von m mit $\Re(\frac{1}{2} \pm m - k) > 0$ so gilt (3), aus Stetigkeitsgründen, auch noch, falls $2m$ ganz ist.

Ich darf also $arg\,\zeta = 0$ voraussetzen.

Ferner nehme ich vorläufig noch an, dasz $\frac{1}{2} \pm m - k \neq 0, -1, -2, \ldots$ ist. Die durch (5) definierte Funktion $\Phi(k, m, a, w)$ besitzt dann die folgende Integraldarstellung [10])

$$\Phi(k, m, a, w) = \frac{1}{2\pi i} \int_T \frac{\Gamma(\frac{1}{2} + m - s)\,\Gamma(\frac{1}{2} - m - s)\,\Gamma(-k + s)}{\Gamma(a + s)\,\Gamma(\frac{1}{2} + m - k)\,\Gamma(\frac{1}{2} - m - k)}\, w^s\, ds.$$

Hierin wird $w \neq 0$ und $|arg\, w| < \pi$ vorausgesetzt. Der Integrationsweg T läuft von $-\infty i + \mu$ nach $\infty i + \mu$ (μ ist eine beliebige reelle Zahl), und zwar auf derartige Weise, dasz die Punkte $k, k-1, k-2, \ldots$ zur linken, die Punkte $\frac{1}{2} \pm m$, $\frac{3}{2} \pm m$, $\frac{5}{2} \pm m, \ldots$ aber zur rechten Seite von T liegen.

Ist $\zeta u \neq 0$, dann hat man also

$$\Phi(k, m, a, \zeta^2 u^2) = \frac{1}{2\pi i} \int_T \frac{\Gamma(\frac{1}{2} + m - s)\,\Gamma(\frac{1}{2} - m - s)\,\Gamma(-k + s)}{\Gamma(a + s)\,\Gamma(\frac{1}{2} + m - k)\,\Gamma(\frac{1}{2} - m - k)}\, \zeta^{2s}\, u^{2s}\, ds.$$

Ich wähle nun den Integrationsweg T derart, dasz $\Re(a + s) > 0$ ist für alle Punkte s von T [11]). Ich erhalte dann [12])

$$\int_0^\infty e^{-u^2}\, \Phi(k, m, a, \zeta^2 u^2)\, u^{2a-1}\, du$$

$$= \frac{1}{2\pi i} \lim_{\substack{\delta > 0 \\ \delta \to 0}} \int_\delta^\infty e^{-u^2} u^{2a-1}\, du \int_T \frac{\Gamma(\frac{1}{2} + m - s)\,\Gamma(\frac{1}{2} - m - s)\,\Gamma(-k + s)}{\Gamma(a + s)\,\Gamma(\frac{1}{2} + m - k)\,\Gamma(\frac{1}{2} - m - k)}\, \zeta^{2s}\, u^{2s}\, ds$$

$$= \frac{1}{2\pi i} \lim_{\substack{\delta > 0 \\ \delta \to 0}} \int_T \frac{\Gamma(\frac{1}{2} + m - s)\,\Gamma(\frac{1}{2} - m - s)\,\Gamma(-k + s)}{\Gamma(a + s)\,\Gamma(\frac{1}{2} + m - k)\,\Gamma(\frac{1}{2} - m - k)}\, \zeta^{2s}\, ds \int_\delta^\infty e^{-u^2}\, u^{2a+2s-1}\, du$$

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[10]) Man vergl.: E. W. BARNES, Proceedings of the London Mathematical Society (2) **5** (1907), S. 65—71.

[11]) Dies ist möglich, wegen $\Re(\frac{1}{2} \pm m + a) > 0$.

[12]) Die Vertauschung der Integrationsfolge ist erlaubt; siehe T. J. I' A. BROMWICH, An Introduction to the Theory of infinite Series, § 177. Man sieht ferner leicht ein, dasz

$$\lim_{\substack{\delta > 0 \\ \delta \to 0}} \int_T \ldots ds \int_\delta^\infty \ldots du = \int_T \ldots ds \int_0^\infty \ldots du$$

ist.

$$= \frac{1}{2\pi i}\int_T \frac{\Gamma(\frac{1}{2}+m-s)\,\Gamma(\frac{1}{2}-m-s)\,\Gamma(-k+s)}{\Gamma(\alpha+s)\,\Gamma(\frac{1}{2}+m-k)\,\Gamma(\frac{1}{2}-m-k)}\,\zeta^{2s}\,ds \int_0^\infty e^{-u^2}\,u^{2\alpha+2s-1}\,du$$

$$= \frac{1}{4\pi i}\int_T \frac{\Gamma(\frac{1}{2}+m-s)\,\Gamma(\frac{1}{2}-m-s)\,\Gamma(-k+s)}{\Gamma(\frac{1}{2}+m-k)\,\Gamma(\frac{1}{2}-m-k)}\,\zeta^{2s}\,ds.$$

Die rechte Seite dieser Beziehung ist aber gleich $\frac{e^{\frac{1}{2}\zeta^2}}{2}\,W_{k,m}(\zeta^2)$ (siehe M. A., § 16.4). Formel (6) ist also bewiesen für den Fall, dasz $\frac{1}{2}\pm m-k \neq 0, -1, -2, \ldots$ ist. Aus Stetigkeitsgründen gilt (6) jedoch auch noch, falls $\frac{1}{2}\pm m-k = 0, -1, -2, \ldots$ ist.

Bemerkung. Formel (3) kann auch folgendermaszen bewiesen worden: Man hat (siehe B. F., S. 183)

$$K_{2m}(2\zeta u) = \tfrac{1}{2}(\zeta u)^{-2m}\int_0^\infty e^{-\tau-\frac{\zeta^2 u^2}{\tau}}\,\tau^{2m-1}\,d\tau.$$

Die rechte Seite von (3) ist also gleich (ich integriere erst nach u)

$$\frac{2\,\zeta^{1-2m}\,e^{-\frac{1}{2}\zeta^2}}{\Gamma(\frac{1}{2}+m-k)\,\Gamma(\frac{1}{2}-m-k)}\int_0^\infty e^{-\tau}\,\tau^{2m-1}\,d\tau\int_0^\infty e^{-\left(1+\frac{\zeta^2}{\tau}\right)u^2}\,u^{-2m-2k}\,du$$

$$= \frac{\zeta^{1-2m}\,e^{-\frac{1}{2}\zeta^2}}{\Gamma(\frac{1}{2}+m-k)}\int_0^\infty e^{-\tau}\,\tau^{2m-1}\left(1+\frac{\zeta^2}{\tau}\right)^{m+k-\frac{1}{2}}\,d\tau$$

$$= \frac{\zeta^{2k}\,e^{-\frac{1}{2}\zeta^2}}{\Gamma(\frac{1}{2}+m-k)}\int_0^\infty e^{-\tau}\,\tau^{m-k-\frac{1}{2}}\left(1+\frac{\tau}{\zeta^2}\right)^{m+k-\frac{1}{2}}\,d\tau.$$

Das letzte Integral ist aber gleich $W_{k,m}(\zeta^2)$ (siehe M. A., § 16.12).

§ 3. Integraldarstellungen für BESSELsche Funktionen.

Bekanntlich hat man [13])

$$K_\nu(z) = \sqrt{\frac{\pi}{2z}}\,W_{0,\nu}(2z) \quad \ldots\ldots\ldots \quad (8)$$

---

[13]) Man hat (siehe I, Formel (17))

$$H_\nu^{(1)}(z) = \sqrt{\frac{2}{\pi z}}\,e^{-i\left(\frac{1}{2}\nu\pi+\frac{1}{4}\pi\right)}\,W_{0,\nu}(-2iz).$$

Hieraus und aus (4) folgt (8).

Die Funktion $K_\nu(\zeta^2)$ besitzt daher, wegen (6) und (3), die folgenden Integraldarstellungen:

$$K_\nu(\zeta^2) = \frac{e^{-\zeta^2}}{\zeta}\sqrt{2\pi}\int_0^\infty e^{-u^2}\,\Phi(0,\nu,\alpha,2\zeta^2u^2)\,u^{2\alpha-1}\,du \quad . \quad . \quad . \quad (9)$$

und

$$K_\nu(\zeta^2) = \frac{4\,e^{-\zeta^2}\cos\nu\pi}{\sqrt{\pi}}\int_0^\infty e^{-u^2}\,K_{2\nu}(2\sqrt{2}\,\zeta u)\,du \quad . \quad . \quad . \quad (10)$$

In (9) bez. (10) wird 2ν nicht ganz und $\Re(\frac{1}{2}\pm\nu+\alpha)>0$, bez. $|\Re(\nu)|<\frac{1}{2}$ vorausgesetzt.

Ferner gilt [14])

$$I_\nu(z)\cos\nu\pi = \frac{1}{2\pi i}\{e^{-\nu\pi i}K_\nu(ze^{-\pi i}) - e^{\nu\pi i}K_\nu(ze^{\pi i})\} \quad . \quad . \quad . \quad (11)$$

Ist 2ν nicht ganz und $\Re(\frac{1}{2}\pm\nu+\alpha)>0$, dann hat man also mit Rücksicht auf (9)

$$\left.\begin{aligned} I_\nu(\zeta^2)\cos\nu\pi = {}& \frac{e^{\zeta^2}}{\zeta\sqrt{2\pi}}\int_0^\infty e^{-u^2}u^{2\alpha-1}\times \\ & \{e^{-\nu\pi i}\Phi(0,\nu,\alpha,2e^{-\pi i}\zeta^2u^2) + e^{\nu\pi i}\Phi(0,\nu,\alpha,2e^{\pi i}\zeta^2u^2)\}\,du. \end{aligned}\right\} \quad . \quad . \quad . \quad (12)$$

Aus (5) folgt aber

$$\frac{1}{\sqrt{2\pi}}\{e^{-\nu\pi i}\Phi(0,\nu,\alpha,we^{-\pi i}) + e^{\nu\pi i}\Phi(0,\nu,\alpha,we^{\pi i})\}$$

$$= \frac{\sqrt{2\pi}\,w^{\frac{1}{2}+\nu}}{\Gamma(\frac{1}{2}-\nu)\,\Gamma(\frac{1}{2}+\nu+\alpha)\,\Gamma(1+2\nu)}\;{}_1F_2(\tfrac{1}{2}+\nu;\ 1+2\nu,\ \tfrac{1}{2}+\nu+\alpha;-w)$$

$$= \frac{2^{\frac{1}{2}-2\nu}\,w^{\frac{1}{2}+\nu}\cos\nu\pi}{\Gamma(1+\nu)\,\Gamma(\frac{1}{2}+\nu+\alpha)}\;{}_1F_2(\tfrac{1}{2}+\nu;\ 1+2\nu,\ \tfrac{1}{2}+\nu+\alpha;-w).$$

Formel (12) geht also über in

$$I_\nu(\zeta^2) = \frac{2^{1-\nu}\,\zeta^{2\nu}e^{\zeta^2}}{\Gamma(1+\nu)\,\Gamma(\frac{1}{2}+\nu+\alpha)}\int_0^\infty e^{-u^2}u^{2\alpha+2\nu}\;{}_1F_2(\tfrac{1}{2}+\nu;\ 1+2\nu,\ \tfrac{1}{2}+\nu+\alpha;-2\zeta^2u^2)\,du; \quad (13)$$

---

[14]) $$I_\nu(z) = e^{-\frac{1}{2}\nu\pi i}J_\nu(ze^{\frac{1}{2}\pi i}),$$

wo $J_\nu(z)$ die BESSELsche Funktion bedeutet. Für (11) vergl. man B. F., S. 80, Formel (17) und (18).

die rechte Seite dieser Beziehung ist nicht sinnlos für $2\nu = 0, \pm 1, \pm 2, \ldots$.[15]) und konvergiert, falls $\Re(\frac{1}{2} + \nu + \alpha) > 0$ ist[16]). Aus der Theorie der analytischen Fortsetzung ergibt sich daher, dasz (13) gilt, falls $\Re(\frac{1}{2} + \nu + \alpha) > 0$ ist.

Nimmt man nun $\alpha = 0$ (also $\Re(\frac{1}{2} + \nu) > 0$), dann erhält man

$$I_\nu(\zeta^2) = \frac{2^{1+\nu}\,\zeta^{2\nu}\,e^{\zeta^2}}{\sqrt{\pi}\,\Gamma(1+2\nu)} \int_0^\infty e^{-u^2} u^{2\nu}\, {}_0F_1(1+2\nu; -2\zeta^2 u^2)\, du \quad . \quad . \quad . \quad . \quad (14)$$

Man hat aber[17])

$$J_\mu(z) = \frac{1}{\Gamma(1+\mu)} \left(\frac{z}{2}\right)^\mu {}_0F_1\left(1+\mu; -\frac{z^2}{4}\right),$$

so dasz aus (14) folgt

$$I_\nu(\zeta^2) = \frac{2}{\sqrt{\pi}}\, e^{\zeta^2} \int_0^\infty e^{-u^2} J_{2\nu}(2\sqrt{2}\,\zeta u)\, du. \quad . \quad . \quad . \quad . \quad (15)$$

Die Integraldarstellungen (13) und (15) für $I_\nu(\zeta^2)$ entsprechen den Relationen (9) und (10) für $K_\nu(\zeta^2)$.

Man bekommt andere einfache Spezialfälle von (9) und (13), wenn man $\alpha = \frac{1}{2}$ nimmt. Es gilt nämlich[18])

$$J_\nu^2(z) = \frac{1}{\Gamma^2(1+\nu)} \left(\frac{z}{2}\right)^{2\nu} {}_1F_2(\tfrac{1}{2}+\nu; 1+\nu, 1+2\nu; -z^2) \quad . \quad (16)$$

und

$$I_\nu^2(z) = \frac{1}{\Gamma^2(1+\nu)} \left(\frac{z}{2}\right)^{2\nu} {}_1F_2(\tfrac{1}{2}+\nu;\ 1+\nu,\ 1+2\nu;\ z^2).$$

Hieraus und aus (5) folgt, falls 2ν nicht ganz ist,

$$\Phi(0, \nu, \tfrac{1}{2}, z^2) = \frac{z\sqrt{\pi}}{2\sin\nu\pi} \{I_{-\nu}^2(z) - I_\nu^2(z)\} \quad . \quad . \quad . \quad . \quad (17)$$

---

[15]) Denn man hat

$$\frac{1}{\Gamma(a+\frac{1}{2})\,\Gamma(c)}\ {}_1F_2(a; 2a, c; w) = \frac{1}{\Gamma(a+\frac{1}{2})\,\Gamma(c)} +$$

$$+ \frac{1}{\Gamma(a+\frac{1}{2})\,\Gamma(c+1)\,.\,1!} \cdot \frac{w}{2} + \frac{a+1}{\Gamma(a+\frac{3}{2})\,\Gamma(c+2)\,.\,2!}\left(\frac{w}{2}\right)^2 +$$

$$+ \frac{a+2}{\Gamma(a+\frac{3}{2})\,\Gamma(c+3)\,.\,3!}\left(\frac{w}{2}\right)^3 + \frac{(a+2)(a+3)}{\Gamma(a+\frac{5}{2})\,\Gamma(c+4)\,.\,4!}\left(\frac{w}{2}\right)^4 + \ldots.$$

[16]) Siehe auch Formel (7).

[17]) Siehe B. F., S. 100.

[18]) Man vergl. B. F., S. 147.

Man hat also wegen (13), (16), (9) und (17)

$$I_\nu(\zeta^2) = 2e^{\frac{\zeta^2}{2}} \int_0^\infty e^{-u^2} J_\nu^2(\zeta u\sqrt{2})\, u\, du \quad . \quad . \quad . \quad . \quad . \quad (18)$$

und

$$K_\nu(\zeta^2) \sin \nu\pi = \pi e^{-\frac{\zeta^2}{2}} \int_0^\infty e^{-u^2} \{I_{-\nu}^2(\zeta u\sqrt{2}) - I_\nu^2(\zeta u\sqrt{2})\}\, u\, du \quad . \quad (19)$$

In (18) bez. (19) wird $\Re(\nu) > -1$, bez. $|\Re(\nu)| < 1$ vorausgesetzt. Die Relationen (15) und (18) waren schon bekannt [19]).

[19]) Siehe B. F., S. 394, Formel (5) und S. 395, Formel (1).

Chemistry. — *Neue Methoden für die Synthese von Glyceriden.* I. Von P. E. VERKADE und J. VAN DER LEE. (Communicated by Prof. J. BÖESEKEN).

(Communicated at the meeting of November 24, 1934).

§ 1. Im Laufe der letzten Jahre ausgeführte Untersuchungen über die Zusammensetzung in der Natur vorkommender Fette und Öle — es sei hier z.B. an Arbeiten von KLIMONT, BÖMER c.s., AMBERGER c.s., SUZUKI c.s., EIBNER c.s. und vor allem an diejenigen von HILDITCH und seinen Mitarbeitern erinnert — zwingen zu der Schlussfolgerung, dass im pflanzlichen und tierischen Organismus eine ausgesprochene Vorliebe für die Bildung *gemischter* Triglyceride, d.h. solcher, die zwei oder drei verschiedene Fettsäuren als Säurekomponenten enthalten, besteht. Namentlich in bezug auf die Samenfette könnte wohl fast bemerkt werden, dass einfache Triglyceride, mit nur *einer* Säurekomponente, allein dann in nennenswerter Menge gebildet werden, wenn keine andere Bindungsweise der zur Verfügung stehenden Fettsäuren möglich ist.

Infolge der Anerkennung dieser Tatsache sieht die Fettchemie sich selbstverständlich vor eine fraglos sehr wichtige, aber auch äusserst umfangreiche und schwierige Aufgabe gestellt. Es wird nun nämlich versucht werden müssen, allmählig für eine grosse Anzahl Fette und Öle, welche den verschiedensten Gebieten des Pflanzen-, bezw. Tierreichs angehören, die Zusammensetzung des Glyceridgemisches möglichst genau kennen zu lernen. Es unterliegt für uns keinem Zweifel, dass hierbei viele Tatsachen und Gesetzmässigkeiten zutage treten werden, welche sich in theoretischer oder in praktischer Hinsicht als bedeutsam erweisen werden; wir denken hier z.B. an Beziehungen zwischen dem Vorkommen bestimmter gemischter

Triglyceride und der Stellung der Fette oder Öle im botanischen, bezw. zoologischen System.

In Zusammenhang mit eventuellen praktischen Anwendungen von Ergebnissen solcher Untersuchungen sei nebenbei bemerkt, dass die BÖMER'sche Methode zur Prüfung von Schweineschmalz auf Zusatz von Talg auf einem Unterschied in der Glyceridstruktur beider Produkte beruht; Schmalz enthält eine kleine Menge β.Palmito-$\alpha\gamma$.distearin, Talg dagegen α.Palmito-$\beta\gamma$.distearin.

Es ist für unseren Zweck nicht nötig, hier eine Übersicht über die schon veröffentlichten Untersuchungen auf dem soeben angedeuteten Gebiet zu geben. Aus einer solchen Übersicht würde sich zeigen, dass man bisher nur ausnahmsweise zu einer vollständigen Aufklärung der Konstitution der isolierten gemischten Triglyceride, d.h. *zu einer Bestimmung der Stellung der verschiedenen Acylgruppen*, übergegangen ist. Dies ist durchaus verständlich: die Abtrennung individueller Triglyceride in einigermassen reinem Zustand, sei es als solche, sei es in der Form von Bromadditionsprodukten, bietet schon überreich Schwierigkeiten. Für die Erwerbung eines möglichst guten Einblickes in die Glyceridstruktur eines Fettes oder Öles und a fortiori für eine etwaige Vergleichung der Struktur verschiedener Fette oder Öle ist jedoch die Kenntnis der vollständigen Konstitution der isolierten Triglyceride wohl selbstredend unerlässlich.

Die Bestimmung der Stellung der verschiedenen Acylgruppen in einem aus einem Naturprodukt isolierten mehrsäurigen Triglycerid wird wohl immer durch Vergleichung dieser Substanz (wenn ungesättigte Säuren als Säurekomponenten vorhanden sind, eventuell ihres Hydrierungsproduktes) mit auf synthetischem Wege erhaltenen Präparaten erfolgen müssen. Durch die schönen Untersuchungen von EMIL FISCHER und seinen Mitarbeitern [1]) stehen vortreffliche Methoden für die Synthese *zweisäuriger* Triglyceride, sowohl symmetrischer als asymmetrischer, schon lange zur Verfügung; in den letzten Jahren sind diese Methoden in einigen Punkten von untergeordneter Bedeutung von KING und seinen Schülern [2]) ergänzt worden. Schön ausgedachte, doch höchst umständliche Wege zur Herstellung *dreisäuriger* Glyceride sind später durch Untersuchungen von BERGMANN und seinen Mitarbeitern [3]) zur Verfügung gekommen; diese Forscher haben in der Tat α. Acetyl-β. (p. nitrobenzoyl) -γ. benzoyl-glycerol synthetisiert. Versuche über die Brauchbarkeit dieser Verfahren für die Synthese dreisäuriger Glyceride, *welche in der Natur auftretende Fettsäuren als Säurekomponenten enthalten*, hat BERGMANN bestimmt angestellt [4]); in dieser Richtung ist jedoch bisher nichts veröffentlicht

[1]) FISCHER, BERGMANN und BÄRWIND, Ber. **53**, 1589 (1920); FISCHER und PFÄHLER, ibid. **53**, 1606 (1920); FISCHER, ibid. **53**, 1621 (1920).

[2]) AVERILL, ROCHE und KING, J. Am. Chem. Soc. **51**, 866 (1929); ROBINSON, ROCHE und KING, ibid. **54**, 705 (1932); MC. ELROY und KING, ibid. **56**, 1191 (1934).

[3]) BERGMANN, BRAND und DREYER, Ber. **54**, 936 (1921); BERGMANN, Z. physiol. Chem. **137**, 27 (1924).

[4]) Vgl. Ber. **54**, 944 (1921).

worden. Es ist diesbezüglich sicher die Annahme berechtigt, dass sich hierbei unüberwindliche experimentelle Schwierigkeiten ergeben haben. Beiläufig sei hier noch auf einen wohl schon von vornherein zum Misslingen verurteilten Versuch von AMBERGER und WIESEHAHN [5]) zur Synthese von β. Oleo-palmitostearin hingewiesen.

Es ist uns nunmehr gelungen, eine recht einfache Methode für die Synthese dreisäuriger Glyceride auszuarbeiten, welche — selbstverständlich abgesehen von experimentellen Schwierigkeiten in bestimmten Fällen, z.B. verursacht durch niedrige Schmelzpunkte der Zwischen- oder Endprodukte — allgemein anwendbar ist und keinerlei Zweifel an der Konstitution der erhaltenen Produkte bestehen lässt. *Bei dieser Synthese werden in bestimmten Fällen* (vgl. §§ 2 und 4) *als Zwischenprodukte zweisäurige $\alpha\gamma$. Diglyceride erhalten.* Soweit uns bekannt, stand eine Methode für die Synthese solcher Substanzen (z.B. α.Palmityl-γ.stearylglycerol) bisher noch nicht zur Verfügung.

Die betreffende Methode wird in dem hier Folgenden nur in Hauptlinien beschrieben, und zwar vornehmlich — wofür wir berechtigten Grund haben — um unsere Prioritätsrechte festzulegen. Die von uns auf diesem Gebiete durchgeführten Untersuchungen werden zu gelegener Zeit anderswo ausführlich besprochen werden.

§ 2. Ausgangspunkt für unsere Synthese dreisäuriger Glyceride bilden die α. Monoglyceride I (wir werden in den Formeln die Acylgruppen mit den Buchstaben D, E und F bezeichnen), welche, ausgehend von Acetonglycerol, nach FISCHER, BERGMANN und BÄRWIND [1]) sehr leicht zugänglich sind. Wir haben die Herstellungsweise dieser Substanzen noch etwas verbessern und dadurch die Ausbeute erhöhen können. Ein unwiderlegbarer Beweis für die α-Stellung der Acylgruppe in diesen Verbindungen ist von BERGMANN und SABETAY [6]) geliefert worden. Das von diesen Forschern auf einem ganz anderen Wege, nämlich ausgehend von 2. Phenyl-5. chloromethyl-oxazolidin, erhaltene Monolaurin, bezw. Monostearin besass nämlich zweifellos eine asymmetrische Struktur, da es nach vorhergehender Spaltung eines der Zwischenprodukte in optisch-aktiver Form erhalten werden konnte, und erwies sich mit einem nach FISCHER, BERGMANN und BÄRWIND bereiteten Präparat als völlig identisch.

Wird ein α. Monoglycerid mit der theoretischen Menge (1 Mol.) Triphenylmethylchlorid (= Tritylchlorid) in Gegenwart von überschüssigem Pyridin oder Chinolin kurze Zeit auf dem Wasserbade erwärmt, dann entsteht mit sehr guter Ausbeute eine *Monotritylverbindung*, der mit fast vollkommener Sicherheit die Struktur II (die Tritylgruppe werden wir in den Formeln immer mit den Buchstaben Tri bezeichnen) zuerkannt werden muss. Die gleiche Verbindung entsteht nämlich als Hauptprodukt bei

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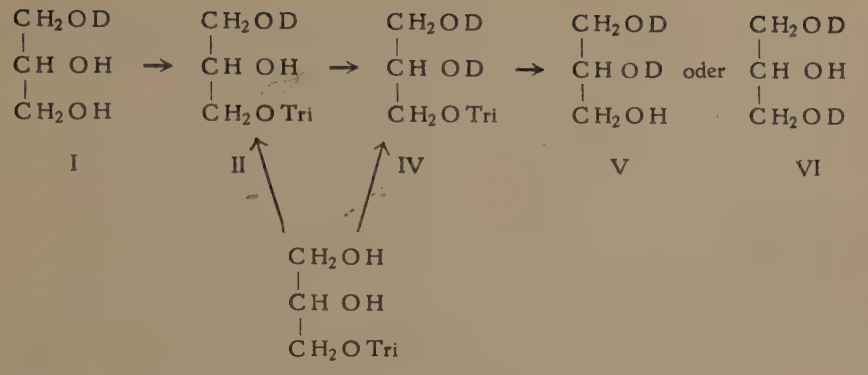
[5]) Z. Untersuch. Lebensm. **46**, 296 (1923).
[6]) Z. physiol. Chem. **137**, 47 (1924).



Hinzufügung einer Lösung von 1 Mol. Acylchlorid D.Cl in Chloroform zu 1 Mol. Monotritylglycerol, gelöst in Chinolin. Die letztgenannte Verbindung (Schmelzpunkt 109-110°), deren Herstellungsweise[7]) wir sehr bedeutend verbessern konnten, besitzt nun so gut wie sicher die Struktur III. Sowohl HELFERICH und SIEBER[8]) als JACKSON und KING[9]) haben nämlich nachgewiesen, dass hieraus durch Benzoylieren und Detritylieren der dabei gebildeten Dibenzoylverbindung $\alpha\beta$. Dibenzoylglycerol (allgemeine Formel V) entsteht; die durchaus sicheren Beweise für die Konstitution der letztgenannten Verbindung können hier unbesprochen bleiben. Daher ist im Monotritylglycerol die Tritylgruppe endständig, es sei denn, dass während der Detritylierung der Dibenzoylverbindung Wanderung einer Benzoylgruppe aus einer α- in die β-Stellung auftritt. Dies ist jedoch wohl sehr unwahrscheinlich. Denn umgekehrt ist gerade die Wanderung von Gruppen aus der β- in die α-Stellung eine bei Glyceriden sehr häufig vorkommende Erscheinung. Ein sehr schönes Beispiel hiervon ist der Übergang von β.- in α. Monopalmitin unter Einfluss verdünnter alkoholischer Salzsäure bei Zimmertemperatur, der kürzlich von STIMMEL und KING[10]) untersucht wurde.

Die Konstitutionsformeln II und III, die wir auf Grund des Obigen glauben annehmen zu müssen, finden eine indirekte und sicherlich nicht kräftige Stütze in einem Ausspruche HELFERICH's[11]), der sich hauptsächlich auf die Erfahrungen gründet, welche dieser Forscher bei seinen Untersuchungen über Tritylverbindungen von Zuckern und nahe verwandten Substanzen machte. Nach ihm sollen nämlich bei dieser Klasse von Polyhydroxylverbindungen unter den angewandten Bedingungen *nur primäre Hydroxylgruppen* mit Tritylchlorid bei Anwesenheit von Pyridin in Reaktion getreten sein. Es ist für unseren Zweck nicht nötig, hier die Zulässigkeit dieses Ausspruchs an dem vollständigen verfügbaren Tat-

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[7]) HELFERICH, SPEIDEL und TOELDTE, Ber. **56**, 766 (1923).
[8]) Z. physiol. Chem. **170**, 31 (1927).
[9]) J. Am. Chem. Soc. **55**, 678 (1933).
[10]) ibid. **56**, 1724 (1934).
[11]) Z. physiol. Chem. **170**, 31 (1927); Z. angew. Chem. **41**, 613, 871 (1928).

sachenmaterial nachzuprüfen. Wir haben den Eindruck, dass er wohl richtig ist und unsere Methode für die Synthese dreisäuriger Glyceride sogar unter dem Einfluss dieses Eindruckes konzipiert.

Aus dem Nachstehenden wird sich zeigen, dass die Konstitution des α. Acyl-monotritylglycerols uns gleichgültig sein kann, solange wir nur Glyceridsynthesen nachstreben. Doch wird selbstredend versucht werden, die Konstitution II näher zu bestätigen. Es liegt auf der Hand, zu diesem Zwecke den Nachweis erbringen zu suchen, das Monotritylglycerol in optische Antipoden spaltbar ist. Auf ganz andere Methoden zur Bestätigung der Konstitutionsformeln II und III hoffen wir später eingehen zu können.

Bei Hinzufügung einer Lösung von 1 Mol. Acylchlorid D.Cl in Chloroform zu 1 Mol. ebenfalls die Acylgruppe D enthaltendem und in Chinolin gelöstem α. Acyl-monotritylglycerol, entsteht mit guter Ausbeute eine Diacyl-monotritylverbindung, welche ebenfalls ausgehend von Monotritylglycerol erhalten werden kann, und der, bei Annahme der Konstitutionsformeln III und II, die Konstitution IV zukommt. Einige Verbindungen dieser Art waren, von Monotritylglycerol ausgehend, schon früher von JACKSON und KING [9]) hergestellt worden, jedoch mit viel geringerer Ausbeute; von der Herstellung der Dibenzoylverbindung ist schon oben die Rede gewesen.

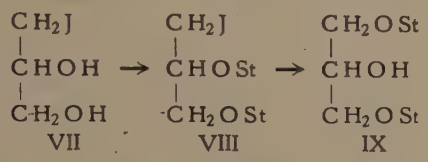
Es wurde bereits mitgeteilt, dass beim Detritylieren von Dibenzoyltritylglycerol und zwar mit Hilfe einer gesättigten Lösung von Bromwasserstoffsäure in Eisessig [8]) oder in Chloroform [9]) $\alpha\beta$. Dibenzoylglycerol entsteht. Dagegen fanden JACKSON und KING [9]), — und wir können dies vollkommen bestätigen —, dass unter ganz denselben Bedingungen aus Dipalmityl-tritylglycerol, bezw. Distearyl-tritylglycerol $\alpha\gamma$. Dipalmitin, bezw. $\alpha\gamma$. Distearin erhalten wird; die symmetrische Konstitution VI dieser letzten Verbindungen folgt mit Sicherheit aus dem Umstande, dass die hieraus bereiteten zweisäurigen Triglyceride nicht mit denjenigen identisch sind, welche ausgehend von dem erforderlichen α. Monoglycerid erhalten werden können. Fraglos findet also in einem dieser beiden Fälle bei der Detritylierung Wanderung einer Acylgruppe statt. Nach unserer oben verteidigten Ansicht, die von JACKSON und KING geteilt wird, findet diese im letztgenannten Falle, also wenn die Acylgruppen Fettsäurereste sind, statt, und daher aus der β- in eine α-Stellung. Derselbe merkwürdige Gegensatz zwischen Benzoyl- und p-Nitrobenzoylgruppen einerseits und Fettsäureresten anderseits wurde bei Detritylierung in der angegebenen Weise von Acyl-ditritylglycerolen konstatiert. Hierbei wurde nämlich β. Benzoylglycerol und β.(p. Nitrobenzoyl)glycerol, dagegen α. Monopalmitin und α. Monostearin erhalten [12]).

Diese von JACKSON und KING zuerst beschriebene Bildungsweise der einsäurigen $\beta\gamma$. Diglyceride ist eng der von FISCHER [13]) angegebenen Her-

[12]) HELFERICH und SIEBER, Z. physiol. Chem. **170**, 31 (1927); **175**, 311 (1928); JACKSON und KING, loc. cit.

[13]) Ber. **53**, 1621 (1920).

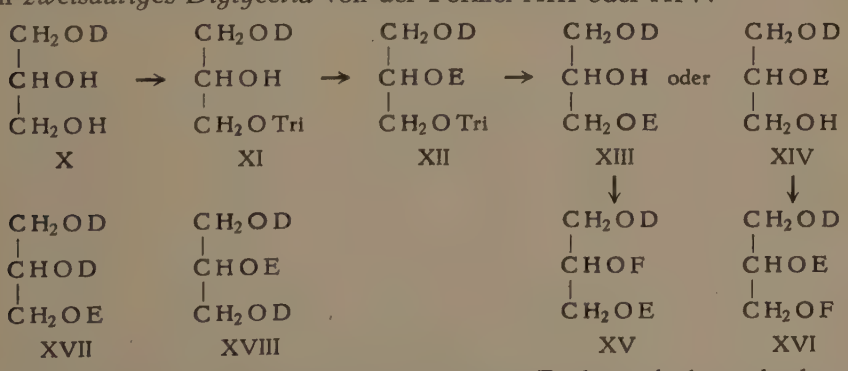
stellungsweise dieser Substanzen verwandt. Ausgehend von Monojodhydrin, dem wohl die Konstitution VII zuerkannt werden muss, wird z.B. die



Distearylverbindung VIII hergestellt, welche durch Kochen mit Silbernitrit in alkoholischer Lösung in $\alpha\gamma$-Distearin IX verwandelt wird. Das Monotritylglycerol ist jetzt von uns zu einer leicht in grossen Mengen zugänglichen Substanz gemacht worden. Es erhebt sich deshalb die Frage, ob die von dieser Substanz ausgehende Bereitung symmetrischer einsäuriger Diglyceride nicht den Vorzug vor dem von FISCHER angegebenen Verfahren verdient.

§ 3. Auf Grund der in § 2 niedergelegten Ausführungen kann nunmehr die folgende einfache Methode für die Synthese dreisäuriger Glyceride angegeben werden.

Ausgehend von dem aus Acetonglycerol und Acylchlorid D.Cl hergestellten α-Monoglycerid X, wird in der oben schon kurz angedeuteten Weise die Monotritylverbindung XI erhalten; für die im nachstehenden Schema dieser Verbindung zuerkannte Konstitution sei nach § 2 verwiesen. Diese Substanz wird in Pyridin oder Chinolin gelöst und bei Zimmertemperatur mit der theoretischen Menge (1 Mol.) des in Chloroform gelösten Acylchlorids E.Cl in Reaktion gebracht. Dem hierbei mit sehr guter Ausbeute entstandenen zweisäurigen Diacyl-monotritylglycerol XII wird darauf, z.B. auf eine der bereits in § 2 genannten Weisen, die Tritylgruppe entzogen. Hierbei entsteht dann, abhängig von dem Auftreten oder Nicht-Auftreten einer Acylverschiebung von der β- nach einer α-Stellung, ein *zweisäuriges Diglycerid* von der Formel XIII oder XIV.



Die Struktur des erhaltenen zweisäurigen Diglycerids kann leicht und mit vollkommener Sicherheit bewiesen werden. Wir werden hier nur eine Methode angeben; vielleicht ergibt sich später noch Gelegenheit auch andere Methoden zu besprechen. Besitzt die erhaltene Substanz die $\alpha\gamma$-Struktur XIII, dann liefert sie bei Einwirkung von 1 Mol. Acylchlorid

D.Cl in der bekannten Weise ein *asymmetrisches* zweisäuriges Triglycerid XVII; hat sie dagegen die $\alpha\beta$-Struktur XIV, so liefert sie bei Einwirkung desselben Acylchlorids ein *symmetrisches* zweisäuriges Triglycerid XVIII. Diese Triglyceride können nun auch mit Hilfe anderer, ursprünglich von EMIL FISCHER und seinen Mitarbeitern herrührenden Verfahren[1]) hergestellt werden. Die Konstitution der auf diese Weise erhaltenen Substanzen steht einwandfrei fest. Die physikalischen Eigenschaften (Schmelzpunkt, Löslichkeit) eines Isomerenpaares sind genügend verschieden[2]) um mit ihrer Hilfe die Identifizierung eines Präparates leicht zu ermöglichen.

Wird das zweisäurige Diglycerid XIII bezw. XIV schliesslich in der üblichen Weise mit 1 Mol. Acylchlorid F.Cl in Reaktion gebracht, dann entsteht das dreisäurige Glycerid XV bezw. XVI. Die Konstitution desselben folgt mit vollkommener Sicherheit aus derjenigen der Verbindung XIII bezw. XIV.

§ 4. Weil die Konstitution des in der soeben angegebenen Weise erhaltenen zweisäurigen Diglycerids immer mit völliger Sicherheit zu bestimmen ist, kann selbstverständlich — wie bereits in § 2 bemerkt wurde — die Konstitution der beiden als Zwischenprodukt auftretenden Monotritylverbindungen uns gleichgültig lassen, solange es sich nur um die Herstellung der genannten Diglyceride oder dreisäuriger Glyceride handelt. Die nunmehr leicht zugänglich gewordenen, *zwei verschiedene Acylgruppen enthaltenden* Diacyl-tritylglycerole bilden jedoch auch sehr brauchbares Material für Untersuchungen in einer ganz anderen Richtung, *falls inzwischen ihre Konstitution vollständig bekannt ist*. Sie können dann nämlich sehr gut dienen für ein näheres Studium der interessanten Erscheinungen, welche bei der Detritylierung der *ein*säurigen Diacyl-tritylglycerole mit einer gesättigten Lösung von Bromwasserstoffsäure in Eisessig oder in Chloroform aufgefunden worden sind und welche wir in § 2 schon kurz besprochen haben. Wir haben schon dargelegt, dass in diesen Verbindungen die Tritylgruppe mit nahezu völliger Sicherheit endständig ist und daher Acylwanderung aus der β- in eine α-Stellung eintritt, wenn beide Acylgruppen Palmityl- oder Stearylgruppen sind, während eine solche Umlagerung ausbleibt, wenn zwei Benzoyl- oder p. Nitrobenzoylgruppen vorhanden sind. Es drängen sich jetzt mehrere Fragen auf, z.B. was geschehen wird, wenn eine Benzoyl- und eine Palmitylgruppe vorhanden sind und zwar in den beiden möglichen Kombinationen (α. Benzoyl-β. palmityl-γ. tritylglycerol und α. Palmityl-β. benzoyl-γ. tritylglycerol)? Wird das Auftreten oder Ausbleiben einer Acylwanderung allein durch die Art der β-ständigen Gruppe bestimmt oder spielt auch die Art der α-ständigen Gruppe hierbei eine Rolle? Wir beabsichtigen in späteren Abhandlungen diese und ähnliche Fragen an Hand von einschlägigen Experimenten zu beantworten.

Laboratorium der Niederländischen Handels-Hochschule.
Rotterdam, November 1934.

Palaeontology. — *Die Variationsstatistische Methode angewandt auf ein groszes Material von Schizoblastus aus dem Perm von Timor und einige neue Anomalien dieser Gattung.* Von H. JANSEN. (Communicated by Prof. H. A. BROUWER).

(Communicated at the meeting of November 24, 1934).

Die Schizoblasten von Timor sind von WANNER in verschiedenen Abhandlungen beschrieben worden, worin er die Arten dieses Genus festlegte (Sieh Literaturangabe). Zu dieser Artentstehung werden Merkmale wie die Zahl der Seitenfurchen zwischen den Deckplättchen des Ambulakrums pro 5 mm, die Breite, Höhe der Theka, des Ambulakrums und der Deltoïdplatte, die Verzierung der Theka, die Höhenlage des grösZten Umkreises verwandt.

Aus altem Material von Basleo [1]) und neuen Aufsammlungen von dort und von der Stelle Niipol (Soempek) [2]), an der EHRAT bereits gesammelt hatte, ergab sich bald, dass sich einige Formen, den oben beschriebenen Merkmalen nach, schwer einteilen lieszen. Während es im allgemeinen nicht möglich ist zu entscheiden ob Standortsvarietäten oder Mutationen vorliegen, kann man mit Hilfe der statistischen Methode oft feststellen ob man mit einer neuen Spezies, Varietät, oder einer schon beschriebenen Art zu tun hat.

Bei der statistischen Untersuchung wurden die folgenden Symbole eingeführt:

A = Anzahl Seitenfurchen auf dem Ambulakrum pro 5 mm
H = Höhe der Theka
B = Breite der Theka
B_1 = Breite der Deltoïdplatte
B_2 = Breite des Ambulakrums
AH ist die halbe Zahl der Seitenfurchen des Ambulakrums.

Diese Symbole wurden auf die Koördinate eingetragen. Die so erhaltenen Punkte wurden selbst nicht angegeben, sondern nur die durch Anäufungen entstandenen Felder.

Für die Interpretation der statistischen Methode sind folgende Regeln maszgebend:

I. Schlieszen sich zwei Felder mit zunehmender Breite zusammen, so ist eine Spezies vorhanden, besonders, wenn die Grenzgebiete beider Felder die meisten Exemplare enthalten. Ist dagegen in beiden Feldern die grösZte Häufigkeit (Frequenz), zentral und nicht peripherisch gelegen, oder berühren sie sich nicht, so sind zwei Spezies vorhanden.

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[1]) Aus der Sammlung der Technischen Hochschule in Delft (Koll. JONKER).

[2]) Sammlung des Geologischen Instituts der Universität Amsterdam.

II. Ist eine Form, z.B. in einem Merkmale sehr wenig, in den übrigen Hauptmerkmalen aber ziemlich oder ganz konstant, so kann man auf eine Varietät schlieszen. Einige Formen, die zwischen zwei Feldern liegen, sind wahrscheinlich als Übergange oder Kreuzungen zu deuten.

Es liegen auch Formen vor, von denen zu wenig Exemplare vorhanden sind, oder deren Variationsbreite so grosz ist, dasz sie für die statistische Methode ungeeignet sind. (z.B. Schizoblastus verbeeki, und pseudodelta). Die folgenden Messungen wurden graphisch dargestellt:

A und H; AH und H/B_2; H_1/H_2 und B_1/B_2; H/B und H_1/B_1 (H_1 = Höhe der Deltoidplate; H_2 der Radialplatte).

Es gaben aber nur die in Fig. 1 und 2 wiedergegebenen Messungen deutliche Resultate. Schon WANNER war es bekannt, dasz es beim

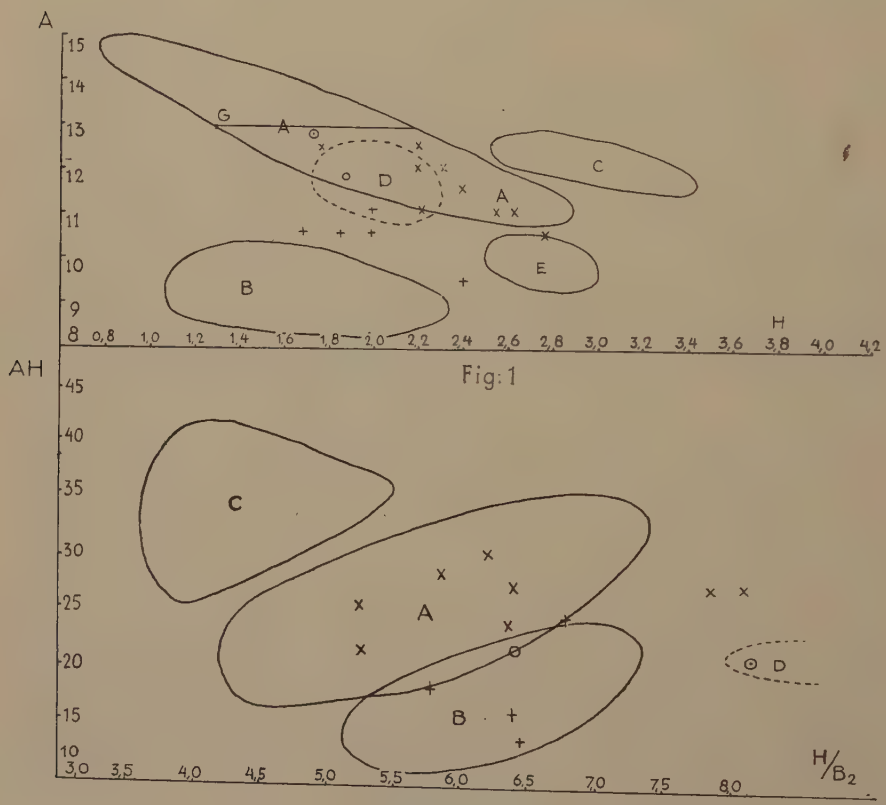

Fig: 1

Fig. 1 en 2.

A = Schizoblastus permicus Feld (160 Messungen).
B = Schizoblastus batheri Feld (25 Messungen).
C = Schizoblastus crassus sp. nov. Feld (15 Messungen).
D = Schizoblastus jonkeri Feld (6 Messungen).
E = Schizoblastus delta Feld (7 Messungen).
G = alte Grenze von Schizoblastus permicus, nach WANNER.
⊙, ○ = Übergang zwischen S. permicus und S. jonkeri.
\+ = Übergang zwischen S. permicus und S. batheri (unverziert).
× = Schizoblastus permicus var. nov. (verziert).

Wachstum von Schizoblastus bestimmte Regeln gab (2. p. 182): Diese konnte ich durch Messungen an einem groszen Material bestätigen. Aus ungefähr 160 Messungen an Schizoblastus permicus ergab sich folgendes Bild (fig. 1—2).

1. Die Anzahl der Seitenfurchen (A) pro 5 mm nimmt mit der Grösze (Höhe der Theka) ab (fig. 1).
2. Das Höhe: Breite Verhältnis der Theka nimmt mit der Höhe zu.
3. Das Höhe: Breite Verhältnis des Ambulakrums nimmt mit der Höhe zu (fig. 2).

Es ergibt sich weiter, dasz bei Schizoblastus permicus, im Gegensatz zu WANNERS Definition (l.p. 44) A kleiner als 13 sein kann (A = 11—15) (fig. 1 sieh G). Ferner ergibt sich statistisch, dasz die groszen schlanken Formen von Niipol und einige von Basleo zu Schizoblastus permicus gehören, da bei einer genügenden Zahl Messungen, das von ihnen eingenommene Feld, immer breiter werdend, sich genau dem Schizoblastus permicus Felde anschlieszt, gerade dort, wo die beiden Felder die gröszten Häufigkeiten enthalten (fig. 1, G). In fig. 2 sind die Felder groszer und kleiner Formen ganz zu einem Felde verschmolzen.

Unter dem Material von Basleo befinden sich dagegen Formen, die nicht ohne weiteres zu Schizoblastus permicus gerechnet werden können.

Die erste hat die folgenden Merkmale (Fig. 1, 2. C).

Die Höhe ist meistens beträchtlich, nämlich durchschnittlich 3.0 cm.

Sollte diese Form Schizoblastus permicus angehören, so könnte man, der oben beschriebenen Entwicklung nach: A = 11 oder weniger erwarten, was jedoch nicht der Fall ist. (A = 12, fig. 1) Auszerdem ist das Verhältnis H/B_2 meistens noch kleiner als bei den kleinsten Schizoblastus permicus, und somit von dem groszen Schizoblastus permicus sehr abweichend (fig. 2). Für das Verhältnis H/B gilt ungefähr dieselbe Betrachtung wie für H/B_2.

Die Dicke der vorliegenden Form ist eines der hervorragendsten Merkmale. Der Namen Schizoblastus crassus sp. nov. scheint daher für diese neue Spezies angebracht.

Fig. 3. Schizoblastus crassus sp. nov. Natürliche Grösze, Orginal in Delft.

Schizoblastus crassus spec. nov.

Höhe: Breite Verhältnis ist 0.9—1.2 (fig. 3).

Die Deltoïdea sind 2—3 mal länger als breit, 1.3—2.5 mal länger als die interradiale Naht zwischen den Lippen der Radialia und dem distalen Ende der Deltoidea. Die Deltoïdea sind an der Radiodeltoidnaht 0.8—1.6 mal breiter als das Ambulakrum, dieses Verhältnis ist bei Schizoblastus permicus durchschnittlich 1.5.

Die Ambulakren und die Basis sind ziemlich tief eingesenkt, die zwei Hälften des Ambulakrums bilden einen stumpfen Winkel. Der Sinuswand ist nicht ausgehöhlt und fällt ziemlich steil gegen das Ambulakrum ab.

Verzierte Formen und Übergänge.

Bisher war noch kein Schizoblastus permicus mit Verzierungen der Theka bekannt. (WANNER; l. p. 72): (Verzierungen der Theka sind nicht vorhanden).

Im Material von Niipol wurden 7 und von Basleo 2 Exemplare gefunden mit ziemlich schwach entwickelten Querleisten, die in jeder Hinsicht dem Schizoblastus permicus gleichen und nicht dem fast immer verzierten Schizoblastus batheri.

Statistisch liegen fast alle diese Abarten im Schizoblastus permicus Felde (fig. 1 u. 2). Auffallend ist, dasz die neuen Formen, sowohl dem Schizoblastus permicus als dem Schizoblastus batheri gegenüber, ziemlich grosz sind (z.B. mittlere Grösze von Schizoblastus permicus und batheri 1.4—1.9 cm neue verzierte Varietät: 1.75—2.75 cm.) Die Verzierung besteht nur aus ziemlich schwach entwickelten Querleisten, welche wie bei Schizoblastus batheri quer über die interradiale Naht hinwegziehen. Die Bedeutung der bei Schizoblastus batheri pseudodelta und permicus var. nov. angetroffene Verzierung ist noch nicht ganz erklärt. Vielleicht sind die Querrippen Ansatzstellen von Muskeln die die Radialia zusammenhielten, zum Teile ist die Verzierung auch dieselbe wie die Anwachsstreifung. Jedenfalls ist die Verzierung allein für die Artbestimmung nicht maszgebend (vergleiche WANNER l. p. 44).

Auch bei Schizoblastus batheri von Basleo kommen Exemplare vor, bei denen die Verzierung primär fehlt. Vielleicht sind es Übergänge (Kreuzungen) zwischen Schizoblastus batheri und permicus, da sie sich in gewissen Merkmalen (z.B.; A) zwischen den Feldern beider Hauptarten befinden (fig. 1 u. 2).

Ebenso gibt es einige Formen, welche auch als Übergänge, nämlich zwischen Schizoblastus permicus und jonkeri zu deuten sind. Sie werden mit einigen Merkmalen im Schizoblastus permicus Felde, und mit andern im Schizoblastus jonkeri Felde angetroffen. Auszerdem liegen die Ambulakren meistens etwas tiefer als bei dem normalen Schizoblastus jonkeri.

Fig. 4.
Schizoblastus verbeeki Wann. var. elongata. var. nov. Vergröszerung $^1/_2$ ×. Original in Amsterdam.

Schizoblastus Verbeeki Wann. var. elongata. var. nova.

Von Basleo stammt noch eine Form, die leider nur in einem verdrückten Exemplar vorliegt, welches viele Ähnlichkeiten mit Schizoblastus verbeeki besitzt, aber viel gröszer und schlanker als der gewöhnliche Schizoblastus verbeeki ist (fig. 4).

$H = 6.5$ $H/B = 1.9$ (bezw. verbeeki: 1.2—1.6) $H/B_2 = 14.4$ (bezw. verbeeki: 6—8).

Wie bei den meisten Exemplaren von Schizoblastus verbeeki ist diese

Form abgestutzt kegelförmig und verdrückt. Der Namen Schizoblastus verbeeki var. elongata dürfte diese Abart am besten bezeichnen.

Meine Ergebnisse über die Verwendungsmöglichkeit der statistischen Methode möchte ich zusammenfassen. Auch die statistische Methode ist nicht ganz objectiv, da sie selbst bei groszem Material abhängig bleibt von der Anzahl und Auswahl der vorgenommenen Messungen. Sie liefert deutliche Resultate bei einzelnen Merkmalen. Bei groszem Material wird sie jedoch ein wertvolles Hilfsmittel zur Klärung und Praecisierung zwischen den einzelnen Formenkreisen liefern.

Anomalien.

Bei der Durchsicht des Materials von vielen Tausenden von Schizoblasten fanden sich auch wieder zahlreiche Anomalien vor, unter welchen:

Von Basleo eine Form, die man mit WANNER (4, p. 19) zur Gruppe II (Excessa) einteilen könnte (fig. 5). Lage der Anomalie in der Theka zwischen r a R unr r p I R Theka mit einem überzähligen, nicht ganz

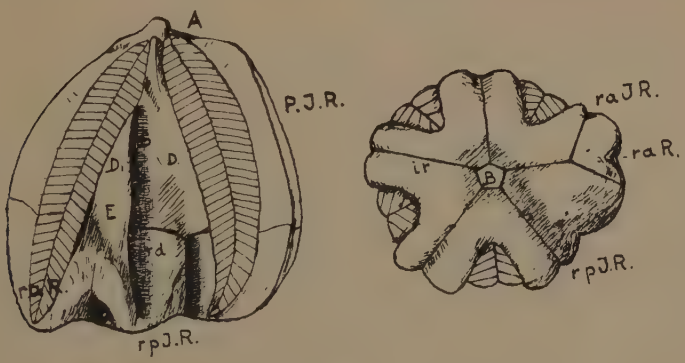

Fig. 5.

Schizoblastus permicus Wanner sechsstrahlig. Orginal in Delft.

A = Anale Öffnung.	ir = Interradiale Naht.
S = Sinus vom sechsten Radius.	rd = Radiodeltoïd Naht.
D_1 = Deltoïd „ „	E = Einsenkung.
B = Basalkranz.	Vergröszerung: 3 ×.

entwickelten Interradius. Dieser besteht aus einem Radiale und Deltoïd. Also ist diese Form ein unregelmäsziger Sechsstrahler, das Ambulakrum ist im abnormalen Sechsten Radius noch nicht entwickelt, wohl aber der Sinus.

Das Deltoïd des sechsten Interradius ist kleiner als die normalen Deltoïdea und am oberen Ende noch nicht ganz ausgewachsen, auch r a I R ist anomal entwickelt. Die Radiodeltoïdnaht von r a I R ist in zwei ungleiche Äste geteilt, der gröszte Ast hat eine sehr schräge Stellung.

Auch die interradiale Naht liegt asymmetrisch auf der Seite von a R. Die zwei interradialen Nähte von r a I R und vom sechsten Interradius treffen noch, bevor sie die Basalia erreichen, zusammen und bilden eine einzige interradiale Naht, so dasz die zwei Äste mit der unteren normalen interradialen Naht Ecken von ung. 130° bilden.

Die anomal vorspringende Lippe von r a R ist nicht nach einwärts gezogen wie die andern, sondern springt vor.

Die Radiodeltoïdnaht im sechsten anomalen Interradius ist nicht ganz entwickelt. Wohl aber ist der anomale Interradius an der Radiodeltoïdnaht und etwas höher vertieft, während das auf der einen Seite gut entwickelte Ambulakrum auf einer kurzen Strecke höher liegt als der Interradius; diese Vertiefung des Interradius läuft nach der Seite des Ambulakrums etwas schräg nach oben.

Bei einer Form von Tonino (Sopaba) ist die Spaltung einer interradialen Naht in zwei interradiale Nähte genau dieselbe. Die zwei Nähte treffen mit den Ambulakren zu beiden Seiten des anomalen Interradius zusammen und zwar auf der Höhe der Radiodeltoïdnaht. Diese letzte läuft anomal schräg nach oben und trifft genau in der Mitte des anomalen Interradius mit einer Längsfurche der Deltoïdplatte zusammen.

Die Radialplatte zwischen den zwei interradialen Nähten ist rautenförmig.

Lage: Anomaler Interradius rechts hinten (rpIR).

Von Niipol stammt eine Form, die sowohl mit den oben beschriebenen Former als auch mit dem von WANNER beschriebenen Typus Fa viele Ähnlichkeiten besitzt. Auch hier treffen zwei interradiale Nähte zusammen, bevor sie den Basalkranz erreichen und bilden dort eine einzige interradiale Naht. Lage: Linker vorderer Interradius anomal mit einer überzähligen Platte l a I R und die zwei Interradii mit anomalen interradialen Nähten bezw. raIR und rpIR. Schlieszlich stammt von Niipol noch eine Form, wobei wie beim Typus A (a—z) das eine Ambulakrum teilweise verkümmert, aber nicht eingeschnürt ist wie bei A, dagegen ist genau die Hälfte eines Ambulakrums obliteriert, so dasz die eine Reihe Deckplättchen noch ganz bewahrt bleibt, die andere Reihe aber und somit auch die V-förmige Anordnung der Form der Ambulakral-plättchen ganz verloren geht.

Ich möchte diese Zeilen nicht schlieszen ohne den Herrn Prof. GERTH in Amsterdam und Prof. WANNER in Bonn zu danken für die vielen Ratschläge, die sie mir bei der Ausrührung dieser Untersuchung haben zu Teil werden lassen.

Das Material wurde mir freundlichst von Herrn Prof. Dr. H. A. BROUWER, Direktor des geologischen Instituts zur Verfügung gestellt. Ihm sei hierfür an dieser Stelle der gebührende Dank gebracht.

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Mathematics. — *Electromagnetism, independent of metrical geometry.* 4. *Momentum and energy; waves.* By D. VAN DANTZIG [1]). (Communicated by Prof. J. A. SCHOUTEN).

(Communicated at the meeting of November 24, 1934).

§ 1. *Introduction.*

A well-known difficulty [2]) in general relativity is: *which is the relation existing between the density* $\mathfrak{S}_i^{\ h}$ *of stress, momentum and energy, and the vector* p_i *of momentum and energy?* This relation should be of a form somewhat like $cp_i = \int \mathfrak{S}_i^{\ 4}\, d\mathfrak{S}$ or $cp_i = \int \mathfrak{S}_i^{\ j}\, d\mathfrak{S}_j$, integrated over a three-dimensional space. Neither of these integrals, however, is invariant, for integration of a vector $\mathfrak{S}_i^{\ j}\, d\mathfrak{S}_j$ presumes addition of vectors in different points, a process which has no meaning, except in Euclidian spaces. Moreover, and apart from the special way in which p_i is to be expressed by $\mathfrak{S}_i^{\ h}$, *a vector like* p_i *cannot exist* [2a]) *at all in a consequent field-theory.* Indeed: a vector must always be applied to a certain point [3]),

[1]) Cf. D. VAN DANTZIG, Electromagnetism, independent of metrical geometry, 1. The foundations, 2. Variational principles and further generalisation of the theory, 3. Mass and motion, these Proceedings, **37** (1934) 521—525; 526—531; 643—652, abbreviated as EM 1, 2, 3.

[2]) Cf. W. PAULI, A. S. EDDINGTON, l.c. EM 1, 523, note [3]).

[2a]) With "exist" we mean here: exist, independent of any choice of coordinates.

[3]) For the transformation-formulae $p_i \rightarrow p_{i'} = A_{i'}^{j}\, p_j$ are only well-defined if it is known, in which point the $A_{i'}^{j} = \partial_{i'}\, \xi^j$ are to be calculated.

whereas p_i should be the total amount of momentum and energy, contained in a *finite volume* and therefore would belong to this *volume* instead of to a definite point. Hence *total* (= integrated) *momentum and energy of a field is not a well-defined notion.*[4])

Nevertheless light-waves exist, in general relativity also, and so does the wave-vector $\varkappa_i$. *But how then can* PLANCK*'s law* $E = h\nu$ *and* EINSTEIN*'s extension* $p_i = h\varkappa_i$ *have a meaning?* It is this problem, which will be solved in this paper.

The result is: *for a plane-polarized monochromatic wave*[5]) $\mathfrak{S}_i^{\ h}$ *degenerates into a product*

$$\mathfrak{S}_i^{\ h} \sim \varkappa_i \mathfrak{W}^h, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$\mathfrak{W}^h = \mathfrak{H}^{hj} \varphi_j \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is the "action-current", used in EM 2 (8). Hence, instead of *first* integrating $\mathfrak{S}_i^{\ h}$ and *then* dividing by $\varkappa_i$ (which should give hc), we must *first* divide by $\varkappa_i$ (which is possible because of (1)) and *then* integrate, so that the law of PLANCK-EINSTEIN takes the invariant form $\int \mathfrak{W}^h d\mathfrak{S}_h = hc$. In the special case of *plane* waves, where the $\varkappa_i$ are *constant numbers*, both forms are equivalent.

Moreover, it will be shown (§ 4) that relations (1) and (2) hold not only for *light-waves*, i. e. waves without current, but also for *waves with current*[6]) (Cf. § 2), supposed that the latter is "vibrating" also, and that $\mathfrak{S}_i^{\ h}$ is replaced by a generalized quantity $\mathfrak{T}_i^{\ h}$, in which terms containing the current and the potentials are included (§ 3). Aside $\mathfrak{s}^i = 0$, i. e. light-waves (Cf. § 5), the other special cases $F_{ij} = 0$ and $\mathfrak{h} = \frac{1}{2} H_{ij} \mathfrak{H}^{ij} = 0$ are remarkable. In these latter cases $\mathfrak{W}^i$ is proportional with the electric current $\mathfrak{s}^i$, whereas in the former case $\mathfrak{W}^i$ is because of (1) $^v/_c$ times the Pointing-vector, together with the energy density. Moreover, $\mathfrak{W}^i$ satisfies the "equation of continuity" $\partial_i \mathfrak{W}^i = 0$ for *arbitrary* single waves as a consequence of the equation of motion (Cf. EM 3, § 4). Apparently $\mathfrak{W}^i$ can take entirely the place (but for a factor $^v/_c$) of the energy-current;

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[4]) Contrary to the *density* of momentum and energy $\mathfrak{S}_i^{\ 4}$ and also to the momentum and energy of a material *point*.

[5]) Shortly: a *single* wave. The wave-front need *not* be plane.

[6]) We do not ask here, what is the exact physical meaning of such waves. It may be sufficient that they are possible solutions of MAXWELL's equations. For a particle in rest, i.e. $\mathfrak{s}^a \neq 0$. the waves are stationary, i.e. $\varkappa_4 \neq 0$.

also for arbitrary single waves. It seems that in the general case, where $\mathfrak{W}^i$ and $\mathfrak{S}^i$ are not proportional, intimate connections with the phenomenon of spin exist.

Finally it will be shown in § 8 that not only MAXWELL's equations, but also the equation of motion and the wave-equations can be brought into a very simple form, invariant under arbitrary transformations in *five* coordinates, but for the condition that the physical quantities are independent of the fifth coordinate. It cannot be decided yet, if this invariance has another than a merely formal meaning.

§ 2. *General single waves.*

A single (i. e. plane-polarized and monochromatic) wave is usually represented by equations of the form

$$\varphi_i = \overset{\circ}{\varphi}_i \sin \Phi, \text{ [7]}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the phase Φ is a linear form in the coordinates ξ^i if the waves are plane, whereas the "amplitudes" $\overset{\circ}{\varphi}_i$ are constant numbers. Both conditions can only hold for special (e. g. CARTESian) coordinates. We will drop the first condition altogether, i. e. we allow Φ to be an *arbitrary* function of the coordinates. Then the wave-vector is

$$\varkappa_i = \partial_i \Phi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

so that $\mathbf{k} \overset{*}{=} (\varkappa_1, \varkappa_2, \varkappa_3)$ [8]) is the ordinary (three-dimensional) wave-vector, $\varkappa_4 \overset{*}{=} -\nu/c = \partial \Phi / \partial ct$. [9]) The condition of constancy of the $\overset{\circ}{\varphi}_i$ cannot be omitted entirely, because (3) would become trivial (e. g. with $\Phi =$ constant). We replace it by

$$\partial_{[i} \overset{\circ}{\varphi}_{j]} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which evidently is satisfied if the $\overset{\circ}{\varphi}_i$ are constant, but is more general and independent of the choice of coordinates. From MAXWELL's equation

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[7]) $h, \ldots, m = 1, 2, 3, 4$; $a, \ldots, g = 1, 2, 3$.

[8]) In order to compare easily our results with the usual ones, we split up some equations into their spacelike and timelike parts with respect to Cartesian coordinates. The symbol $\overset{*}{=}$ denotes that the equations are not generally invariant. In space the ordinary vector-symbolism will be used. Vectors will be denoted by fat letters. We must, however, keep in mind that **E**, **H**, **A**, **k** are really covariant vectors, i.e. pairs of *planes*, whereas **B**, **D**, **I**, **W** are covariant *bivectors*, i.e. tubes (or contravariant vector densities, i.e. ordinary vectors per volume).

[9]) We measure phases in *radians*, not in circonferences. Hence our ν is usually called $2\pi\nu$. We use also DIRAC's h, i. e. PLANCK's h, divided by 2π.

$F_{ij} = 2\,\partial_{[i}\varphi_{j]}$ (Cf. EM 2 (1) II) and (3) follows $F_{ij} = 2\,(\partial_{[i}\mathring{\varphi}_{j]}\,\sin\Phi + 2\,\varkappa_{[i}\mathring{\varphi}_{j]}\cos\Phi$. Hence (5) expresses the condition that the bivector F_{ij} is entirely a consequence of the *wave-character* of the field only.

In a part of space-time, where is nothing but light, we have $\mathfrak{s}^i = 0$. It seems however natural, because of the fargoing analogy of MAXWELL's equation $\mathfrak{s}^i = \partial_j \mathfrak{H}^{ij}$ (Cf. EM 2 (1) I) with II (see above), to consider also the more general case, where $\mathfrak{s}^i$ and $\mathfrak{H}^{ij}$ shall also be "waving" functions:

$$\mathfrak{H}^{ij} = \mathring{\mathfrak{H}}^{ij}\,\sin\Phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where the condition analogous to (5) will be

$$\partial_j \mathring{\mathfrak{H}}^{ij} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence such a generalized wave is characterized by

$$\left.\begin{aligned} \varphi_i &= \mathring{\varphi}_i\,\sin\Phi\,;\ \mathfrak{H}^{ij} = \mathring{\mathfrak{H}}^{ij}\,\sin\Phi\,;\\ F_{ij} &= \mathring{F}_{ij}\cos\Phi\,;\ \mathfrak{s}^i = \mathring{\mathfrak{s}}^i\cos\Phi\,; \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$\boxed{F_{ij} \sim 2\,\varkappa_{[i}\varphi_{j]} \quad ; \quad \mathfrak{s}^i \sim \mathfrak{H}^{ij}\,\varkappa_j\ ^{10}).} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Splitting up (9) into space- and time-components, we get

$$\left.\begin{aligned} \mathbf{B} &\overset{*}{\sim} \mathbf{k}\times\mathbf{A} \quad ; \quad \mathbf{E} \overset{*}{\sim} -\mathbf{k}\varphi + {}^{\nu}/_{c}\,.\,\mathbf{A}\\ {}^{1}/_{c}\,\mathbf{I} &\overset{*}{\sim} \mathbf{k}\times\mathbf{H} + {}^{\nu}/_{c}\,\mathbf{D} \quad ; \quad \varrho \overset{*}{\sim} \mathbf{k}\,.\,\mathbf{D} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (10)$$

Hence the direction of **B** is parallel with the intersection of **E** and the wave-front **k**. [11])

The equation of motion $F_{ij}\,\mathfrak{s}^j = 0$ (Cf. EM 3 (36)) becomes here (by exclusion of the trivial case $\varkappa_i = 0$, i. e. $\Phi =$ constant) by means of (9):

$$\varphi_j\,\mathfrak{H}^{jk}\,\varkappa_k = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

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[10]) We use the symbol $\sim$ to indicate that only the *amplitudes* of both members are equal. The phases in both members of (10) differ by $\pi/2$.

[11]) In the metrical theory the relations $\mathbf{E}\,.\,\mathbf{B} = 0$ and $\mathbf{k}\,.\,\mathbf{B} = 0$ would be interpreted by saying that **E** and **k** (i.e. the contravariant vectors orthogonal to the planes of **E** and of **k** respectively) were orthogonal to **B**. Scalar products are built with $+$-signs.

Now the "action-current" (2) becomes here

$$\mathfrak{W}^i = \mathring{\mathfrak{H}}^{ij} \mathring{\varphi}_j \sin^2 \Phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

or, if $\mathbf{W} \overset{*}{=} (\mathfrak{W}^1, \mathfrak{W}^2, \mathfrak{W}^3)$ and $\Omega \overset{*}{=} \mathfrak{W}^4$ are the space- and time-components of $\mathfrak{W}^i$:

$$\mathbf{W} \overset{*}{=} \mathbf{A} \times \mathbf{H} + \varphi \mathbf{D} \quad ; \quad \Omega \overset{*}{=} \mathbf{A} \,.\, \mathbf{D} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

From (12) follows by (5) and (7):

$$\partial_i \mathfrak{W}^i = 2 \varkappa_i \mathring{\mathfrak{H}}^{ij} \mathring{\varphi}_j \sin \Phi \cos \Phi \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Hence the equation of motion (11) takes the form of a *conservation-law*:

$$\partial_i \mathfrak{W}^i = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

We shall see later (§ 5, 6) that (15) is the invariant form of the law of conservation of momentum and energy[12]). It expresses the fact *that the integral*

$$w = \int \mathfrak{W}^i \, d\mathfrak{S}_i \,, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

extended over any space-like section through space-time, is constant. This holds also if the section is taken through a *part* of space-time, bounded by a three-dimensional tube (e.g. a moving box), such that at its boundary

$$\mathfrak{W}^i \, d\mathfrak{S}_i = \mathfrak{H}^{ij} \varphi_j \, d\mathfrak{S}_i = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

This condition will surely be satisfied if $\mathfrak{H}^{ij} \, d\mathfrak{S}_j = 0$. Then we have also $\mathfrak{s}^i \, d\mathfrak{S}_i = 0$, i. e. the walls of the box are *impenetrable for charges*[13]). Also (17) will be satisfied if $\varphi_{[i} \, d\mathfrak{S}_{j]} = 0$. Then we have also $\mathfrak{F}^{ij} \, d\mathfrak{S}_j = 0$,[14]) which means in the case of light-waves that the walls are *perfect mirrors*[15]). Generally we may interpret (17) as *impenetrability of the boundary against energy.*

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12) It is remarkable that also the equation of motion of *point*-mechanics (EM3 (14)) is equivalent with the conservation-law EM3 (18).

13) However, the condition $\mathfrak{s}^i \, d\mathfrak{S}_i = 0$ is *not* sufficient, except if $\mathfrak{W}^i$ and $\mathfrak{s}^i$ are proportional.

14) Indices are always raised and lowered by means of the quadrivector-densities $\mathfrak{E}^{hijk}$, $\mathfrak{E}'_{hijk}$, introduced in EM1, p. 524. Cf. also my paper The fundamental equations of electromagnetism, independent of metrical geometry, Proceedings Cambridge Phil. Soc. **30** (1934) 421—427, cited as F E.

15) At the boundary both $\mathfrak{F}^{ij} \, d\mathfrak{S}_j$ and $\mathfrak{H}^{ij} \, d\mathfrak{S}_j$ must be the same for both media. In the walls of the box $\mathfrak{F}^{ij}$ must be zero. $\mathfrak{H}^{ij}$ must not, because of $\mathfrak{s}^i \neq 0$ in matter.

As w/c has the dimensions of an action, the condition

$$\boxed{w = \int \mathfrak{W}' \, d\mathfrak{S}_i = n\,h\,c}\ ^{16}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

is of *exactly* the same nature as the condition

$$s = \int \mathfrak{s}' \, d\mathfrak{S}_i = n'\,e. \ ^{16}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Whereas (19) expresses the fact that the box contains a finite number of indivisible charges (electrons, etc.), (18) will express the fact that it contains a finite number of indivisible "atoms of action". Indeed, we shall see in § 4 that (18) is equivalent with the law of PLANCK-EINSTEIN.

§ 3. *Generalized stress, momentum and energy.*

The ordinary stress-momentum-energy-affinor-density is

$$\mathfrak{S}_i^{\ h} = + F_{ik}\,\mathfrak{H}^{hk} - \tfrac{1}{4}\,A_i^h\,F_{jk}\,\mathfrak{H}^{jk} \ ^{17}) \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Because of the analogy between MAXWELL's equations I and II it seems natural to extend it with terms $c_1\,\varphi_i\,\mathfrak{F}^h + c_2\,A_i^h\,\varphi_j\,\mathfrak{F}^j$. In order to obtain the right value for the energy-density (time-time-component) we must take $c_1 = 1$, $c_2 = -\tfrac{1}{2}$. Then instead of (20) we get:

$$\mathfrak{T}_i^{\ h} = F_{ik}\,\mathfrak{H}^{hk} + \varphi_i\,\mathfrak{F}^h - \tfrac{1}{2}\,A_i^h\,(\tfrac{1}{2}\,F_{jk}\,\mathfrak{H}^{jk} + \varphi_j\,\mathfrak{F}^j) \quad . \quad . \quad . \quad (21)$$

In particular we have

$$-\mathfrak{T}_4^{\ 4} \overset{*}{=} \tfrac{1}{2}\,(\mathbf{E}\,.\,\mathbf{D} + \mathbf{B}\,.\,\mathbf{H} + {}^1/_c\,\mathbf{I}\,.\,\mathbf{A} + \varrho\,\varphi) \quad . \quad . \quad . \quad . \quad (22)$$

Hence to the ordinary terms $-\mathfrak{S}_4^{\ 4}$, which belong to the energy contained in empty space come two new terms which constitute the part of the energy, contained in the charges, viz. the electrostatic energy-density $\tfrac{1}{2}\,\varrho\,\varphi$ and the density of the "self-potential" of the current $1/2\,c\,.\,\mathbf{I}\,.\,\mathbf{A}$. Also we have from (21):

$$\mathfrak{T}_a^{\ 4} \overset{*}{=} (\mathbf{D} \times \mathbf{B} + \varrho\,.\,\mathbf{A})_a \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Here ${}^1/_c\,\mathbf{D} \times \mathbf{B}$ and ${}^\varphi/_c\,\mathbf{A}$ are the well-known expressions for the density of the momentum of the field and of the charges respectively. In

$$-\mathfrak{T}_4^{\ a} \overset{*}{=} (\mathbf{E} \times \mathbf{H} + {}^\varphi/_c\,.\,\mathbf{I})^a \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

---

16) n and n' are arbitrary integers.

17) A_i^h is the unity-affinor; its components are $= 1$ for $i = h$, and $= 0$ for $i \neq h$.

the first term is POINTING's vector, whereas the second is $\varrho\,\varphi\,\mathfrak{v}/c$ [18]), i.e. the energy, transported by the charges. Finally, we see that the charges exert stresses, analogous to the MAXWELLian ones.

Because of the identity [19])

$$F_{ik}\,\mathfrak{H}^{hk} + H_{ik}\,\mathfrak{F}^{hk} = \tfrac{1}{2}\,A_i^h\,F_{jk}\,\mathfrak{H}^{jk} = \tfrac{1}{2}\,A_i^h\,H_{jk}\,\mathfrak{F}^{jk}, \quad . \quad . \quad . \quad (25)$$

holding for two *arbitrary* bivectors F_{ij}, H_{ij} [20]) we can write $\mathfrak{T}_i^{\cdot h}$ also in the form

$$\mathfrak{T}_i^{\cdot h} = -\,H_{ik}\,\mathfrak{F}^{hk} + \varphi_i\,\mathfrak{F}^h + \tfrac{1}{2}\,A_i^h\,(\tfrac{1}{2}\,H_{jk}\,\mathfrak{F}^{jk} - \varphi_j\,\mathfrak{F}^j). \quad . \quad . \quad (26)$$

where the coefficient of A_i^h is equal to $\mathfrak{W}$. [21])

§ 4. *The law of* PLANCK-EINSTEIN.

Now let us consider a single wave as defined in § 2. Substitution of (8), (9) in (26) gives at once by (12):

$$\boxed{\mathfrak{T}_i^{\cdot h} \sim \varkappa_i\,\mathfrak{W}^h} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Hence in the special case when the wave is *plane* (with respect to certain, e. g. CARTESian, coordinates), i. e. if the $\varkappa_i$ are constants, we can write the condition (18) in the form

$$c\,p_i \overset{*}{=} \int \mathfrak{T}_i^{\cdot h}\,d\mathfrak{S}_h \overset{*}{=} \varkappa_i \int \mathfrak{W}^h\,d\mathfrak{S}_h = n\,h\,\varkappa_i \quad . \quad . \quad . \quad (28)$$

which is the law of PLANCK-EINSTEIN. However, it is to be noted that $\mathfrak{W}^i = \mathring{\mathfrak{W}}^i\,sin^2\Phi$, whereas $\mathfrak{T}_i^{\cdot h} = \mathring{\mathfrak{T}}_i^{\cdot h} sin\,\Phi\,cos\,\Phi$. Hence the general condition (18) may only be brought into the special form (28), if the phase-factor in $\mathfrak{T}_i^{\cdot h}$ is changed from $sin\,\Phi\,cos\,\Phi$ into $sin^2\Phi$. This now is exactly what is done in the usual theory, where only the part $\mathfrak{S}_i^{\cdot h}$ of $\mathfrak{T}_i^{\cdot h}$ is considered and where the $\mathfrak{H}^{ij}$ are replaced by $\mathfrak{g}^{ik}\,\mathfrak{g}^{jl}\,F_{kl}$ which have with $\mathfrak{H}^{ij}$ a difference in phase of $\frac{1}{2}\,\pi$.

Hence we have proved that *the ordinary quantum-condition (28) is a special form of our condition (18)* which is of a much more general nature and, moreover, invariant under arbitrary transformations of coordinates.

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[18]) $\mathfrak{v} = 1/\varrho$! is the velocity of the charges.

[19]) Cf. [14]). It is easily verified by means of the identities, given in FE, p. 425, footnote.

[20]) A special case of (25) is:

$$H_{ik}\,\mathfrak{H}^{hk} = \tfrac{1}{4}\,A_i^h\,H_{jk}\,\mathfrak{H}^{jk}$$

[21]) Cf. EM2 (7). In (21) the corresponding coefficient was equal to $-\,\mathfrak{H}$, Cf. EM3 (40).

§ 5. *The case* $\mathfrak{s}^i = 0$ *(light).*

From equations (9), (11) follow some identities which will often be used:

$$\left.\begin{aligned} &\mathfrak{F}^{ij}\,\varkappa_j = 0,\ \mathfrak{F}^{ij}\,\varphi_j = 0,\ \mathfrak{s}^i\,\varkappa_i = 0,\ \mathfrak{s}^i\,\varphi_i = 0,\ F_{ij}\,\mathfrak{H}^{ij} = 0, \\ &\mathfrak{W}^i\,\varkappa_i = 0,\ \mathfrak{W}^i\,\varphi_i = 0,\ F_{ij}\,\mathfrak{W}^i = 0,\ F_{ij}\,\mathfrak{s}^i = 0,\ F_{ij}\,\mathfrak{F}^{hj} = 0. \end{aligned}\right\} \quad (29)$$

Now let us consider a light-wave, determined by

$$\mathfrak{s}^i \sim \mathfrak{H}^{ij}\,\varkappa_j = 0 \quad (30)$$

In particular we have by (1):

$$\mathfrak{W}^i \overset{*}{\sim} -{}^{c}/_{v}\,\mathfrak{S}_4{}^{i} \quad (31)$$

i. e. the action-current is proportional with the combination of the POINTING-vector $\mathbf{S} = \mathbf{E} \times \mathbf{H}$, and the energy-density $\mathfrak{T} = -\mathfrak{S}_4{}^{4}$. Hence in this case (15) is equivalent with the law of conservation of momentum and energy. By splitting up (30) and (31) we find with the aid of (9) and (11):

$$\left.\begin{aligned} &-{}^{v}/_{c}\,\mathbf{D} \overset{*}{\sim} \mathbf{k} \times \mathbf{H}, \quad \mathbf{k}\,.\,\mathbf{D} \overset{*}{\sim} 0, \quad \mathbf{W} \overset{*}{\sim} -{}^{c}/_{v}\,\mathbf{S} = {}^{c}/_{v}\,\mathbf{E} \times \mathbf{H}, \\ &\Omega \overset{*}{\sim} {}^{c}/_{v}\,\mathfrak{T} = -{}^{v}/_{c}\,\mathbf{k}\,.\,(\mathbf{H} \times \mathbf{A}). \end{aligned}\right\} \quad (32)$$

With respect to the geometrical representation, mentioned in [8]) we remark that the initial plane of **k** is the wave-front, the initial plane of **E** is the polarization-plane, the intersection of the initial planes of **E** and **H** is the light-ray **W**. The vibrating electric and magnetic vector which are usually considered are **B** and **D** (and not **B** and **E**, or **H** and **D**); their directions are contained in **k**. In the special case of empty space the three planes of **k**, **E** and **H** form an orthogonal system.

§ 6. *The cases* $F_{ij} = 0$ *and* $\mathfrak{h} = 0$.

A second special case is given by

$$F_{ij} = 2\,\varkappa_{[i}\,\varphi_{j]} = 0 \quad (33)$$

Then a scalar λ exists, such that

$$\varphi_i = \lambda\,\varkappa_i \quad (34)$$

Then from (9) and (11) follows:

$$\mathfrak{W}^h = \lambda\,\mathfrak{s}^h, \quad (35)$$

i. e. the action-current is proportional with the electric current. As the latter in this case is proportional with the energy-current, (15) again is equivalent with the law of conservation of energy and momentum. Substitution of (35) in (18), (19) shows (taking the case $n = n' = 1$) that the mean value $\bar{\lambda}$ of λ is

$$\bar{\lambda} = hc/e. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Hence we see that

$$1/hc \,.\, \mathfrak{W}^h \sim 1/e \,.\, \mathfrak{s}^h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

may be considered as the probability-current. Note, however, that both sides of (37) differ by a phase-factor $sin^2 \Phi/cos \Phi$, the period of vibration of $\mathfrak{W}^h$ being twice that of $\mathfrak{s}^h$.

If, according to EM3 (33), $p_i = {}^e/_c \,.\, \bar{\varphi}_i$ is interpreted as the momentum and energy of the particle in the sense of *point*-mechanics, we find from (34), (36), supposing $\varkappa_i$ to be approximately constant:

$$p_i = h \bar{\varkappa}_i \; ^{22}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

From (9), (11) follows by the aid of (25), (29):

$$2 \mathfrak{s}^{[h} \mathfrak{W}^{i]} = \mathfrak{H}^{hj} \mathfrak{H}^{ik} F_{jk} = - \mathfrak{H}^{hj} \mathfrak{F}^{ik} H_{jk} = \mathfrak{h} \mathfrak{F}^{hi} \quad . \quad . \quad . \quad (39)$$

where

$$\mathfrak{h} = - \tfrac{1}{4} H_{ij} \mathfrak{H}^{ij} \overset{*}{=} \mathbf{H} \,.\, \mathbf{D} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

Hence an equation of the form (35) holds not only in the case $F_{ij} = 0$, but also in the case

$$\mathfrak{h} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

(and in no other one). From (41) follows easily (Cf. [20]) and (9))

$$H_{ij} \mathfrak{s}^j = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

Hence a contravariant vector u^i exists, such that

$$\mathfrak{H}^{ij} = 2 \, u^{[i} \mathfrak{s}^{j]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

---

22) For $F_{ij} \neq 0$ the p_i of point-mechanics will *not* be proportional with $\varkappa_i$. This seems to contradict (28). However, it is to be noted that a *single* wave will *not* have the character of a material point, even if it bears charge, so that it is not to be expected that it will have analogous properties. The consistency of (28) and (38) shows that for $F_{ij} = 0$ this may be the case.

As we may without loss of generality assume $u^4 \overset{*}{=} 0$, (43) gives by splitting up:

$$\mathbf{H} \overset{*}{=} {}^1/_c\, \mathbf{u} \times \mathbf{l}; \qquad \mathbf{D} \overset{*}{=} -\varrho\, \mathbf{u} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

i.e. $-\mathbf{D}$ and $\mathbf{H}$ have the character of an electric and magnetic moment [23]). Of course the conclusions (36), (37) drawn from (35) remain also valid in the case $\mathfrak{h} = 0$.

§ 7. *The general case.*

Now let us suppose $\mathfrak{s}^i \neq 0$, $F_{ij} \neq 0$, $\mathfrak{h} \neq 0$. Putting for some arbitrary value of λ

$$z^i = -{}^1/_{\mathfrak{h}} \cdot (\mathfrak{W}^i - \lambda\, \mathfrak{s}^i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

we get from (39):

$$\mathfrak{F}^{hi} = 2\, z^{[h}\, \mathfrak{s}^{i]} \quad [24]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Without loss of generality we may assume $z^4 \overset{*}{=} 0$. By extending the integrals (18), (19) over a space $t =$ constant we then find $\int \mathfrak{h}\, z^i\, d\mathfrak{S}_i = 0$ hence $\overline{\lambda} = hc/e$, i.e. (36). Splitting up (46) we get

$$\mathbf{B} \overset{*}{=} \varrho\, \mathbf{z}, \qquad \mathbf{E} \overset{*}{=} {}^1/_c\, \mathbf{z} \times \mathbf{l} \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

Hence $\mathbf{B}$ has the character of an electric, $\mathbf{E}$ that of a magnetic moment (not inversely!) [23]). The vector $\mathbf{z}$ does not bear a phase-factor. From (39) follows also

$$\mathfrak{F}^{hi} = 2\, z^{[h}\, \mathfrak{W}^{i]}/\lambda \overset{*}{=} 2\, y^{[h}\, \mathfrak{T}_4^{i]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

where $y^h \overset{*}{=} -{}^c/_{\nu\lambda} \cdot z^h$, so that $\mathbf{B}$ and $\mathbf{E}$ have also the character of a static moment and of a moment of momentum respectively [23]).

Evidently the physical meaning of these waves, except in the cases $\mathfrak{s}^i = 0$ and $F_{ij} = 0$ is still very mysterious and rather doubtful.

§ 8. *Five-dimensional formalism.*

If we write

$$\left.\begin{aligned} \mathcal{F}_{ijk} &= -s_{ijk}, \qquad \mathcal{F}_{ij5} = F_{ij} \\ \mathcal{H}_{ij} &= H_{ij}, \qquad \mathcal{H}_{i5} = \varphi_i, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

[23]) I renounce here trying to interpret these relations and to connect them with the spin of electrons, as such an interpretation would be rather haphazard in this stadium.

[24]) An equation of the form (46) exists *always* as a consequence of the equation of motion $F_{ij}\, \mathfrak{s}^j = 0$. For $\mathfrak{h} = 0$, however, z^i cannot be expressed in the form (45).

MAXWELL's equations EM2 (1 I, II) may be subsumed into one set, viz.

$$3\,\partial_{[\mu}\,\mathcal{H}_{\lambda\varkappa]} = \mathcal{F}_{\mu\lambda\varkappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

$\iota, \varkappa, \lambda, \mu, \ldots, = 1, 2, 3, 4, 5)$, if, moreover, we put

$$\partial_5 H_{ij} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

On the other hand the relation (50) between a bivector and a trivector in five-dimensional space, together with condition (51) leads to a set of equations of the MAXWELL-form. [25]) Raising and lowering indices with the five-vector-densities $\mathfrak{E}^{\iota\varkappa\lambda\mu\nu}$, $\mathfrak{E}'_{\iota\varkappa\lambda\mu\nu}$, defined by $\mathfrak{E}^{12345} = 1$, $\mathfrak{E}'_{12345} = 1$, we have

$$\left.\begin{aligned} \mathfrak{F}^{ij} &= \mathfrak{F}^{ij}, \qquad \mathfrak{F}^{i5} = -\mathfrak{s}^i \\ \mathfrak{H}^{ijk} &= -\varphi^{ijk}, \qquad \mathfrak{H}^{ij5} = \mathfrak{H}^{ij} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

The equation of motion takes the very simple form

$$\mathfrak{F}^{[\varkappa\lambda}\,\mathfrak{F}^{\mu\nu]} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

or also $\mathfrak{F}^{\varkappa\lambda}\,\mathcal{F}_{\varkappa\lambda\mu} = 0$ (which is equivalent with (53)). Indeed (53) splits up into $F_{ij}\,\mathfrak{s}^j = 0$ which is the equation of motion, and $F_{[ij}\,F_{kl]} = 0$, which is a consequence of it.

The action-density is

$$\mathfrak{W} = \tfrac{1}{4}\,\mathcal{H}_{\lambda\mu}\,\mathfrak{F}^{\lambda\mu} = \mathfrak{W} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

The generalized affinor-density $\mathfrak{T}_i^{\,h}$ of stress, momentum and energy is the space-time part of

$$\mathcal{T}_\lambda^{\,\varkappa} = -\mathcal{H}_{\lambda\mu}\,\mathfrak{F}^{\varkappa\mu} + \mathcal{H}_\lambda^{\varkappa}\,\mathfrak{W} \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

The components are

$$\left.\begin{aligned} \mathcal{T}_i^{\,h} &= \mathfrak{T}_i^{\,h}, \qquad \mathcal{T}_5^{\,h} = \mathfrak{F}^{hj}\,\varphi_j, \\ \mathcal{T}_i^{\,5} &= -H_{ij}\,\mathfrak{s}^j, \qquad \mathcal{T}_5^{\,5} = +\tfrac{1}{4}\,F_{ij}\,\mathfrak{H}^{ij} + \tfrac{1}{2}\,\varphi_i\,\mathfrak{s}^i = -\mathfrak{H}. \end{aligned}\right\} \quad . \quad . \quad . \quad (56)$$

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[25]) Another five-dimensional formalism which is possible is obtained by putting f. i.

$$\mathcal{F}_{ij} = F_{ij} \quad , \quad \mathcal{F}_{i5} = -\varphi_i \quad , \quad \partial_5 F_{ij} = F_{ij}$$
$$\mathcal{H}_{ijk} = s_{ijk} \quad , \quad \mathcal{H}_{ij5} = H_{ij} \quad , \quad \partial_5 s_{ijk} = -s_{ijk}.$$

Then MAXWELL's equations become

$$\partial_{[\nu}\,\mathcal{F}_{\mu\lambda]} = 0 \quad , \quad \partial_{[\nu}\,\mathcal{H}_{\mu\lambda\varkappa]} = 0.$$

In the case of waves, determined by

$$\left.\begin{aligned} &\mathfrak{H}_{\lambda\mu} = \overset{\circ}{\mathfrak{H}}_{\lambda\mu} \sin\Phi, \qquad \mathfrak{F}_{\varkappa\lambda\mu} = \overset{\circ}{\mathfrak{F}}_{\varkappa\lambda\mu} \cos\Phi \\ &\partial_{[\nu} \overset{\circ}{\mathfrak{H}}_{\mu\lambda]} = 0, \qquad \partial_{[\nu} \overset{\circ}{\mathfrak{F}}_{\mu\lambda\varkappa]} = 0 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (57$$

it becomes always

$$\mathfrak{T}_{\lambda}^{\varkappa} = k_{\lambda}\, \mathfrak{W}^{\varkappa} \cot\Phi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

with

$$\left.\begin{aligned} &\mathfrak{W}^{\varkappa} = \tfrac{1}{4}\, \mathfrak{H}^{\varkappa\lambda\mu}\, \mathfrak{H}_{\lambda\mu} \\ &\mathfrak{W}^{i} = \mathfrak{W}^{i}, \quad \mathfrak{W}^{5} = \tfrac{1}{4}\, \mathfrak{H}^{ij}\, H_{ij} = -2\mathfrak{h} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (59)$$

$$k_{\lambda} = \partial_{\lambda} \Phi \qquad k_{i} = \varkappa_{i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

The theory treated in § 2—7 belongs to the special case $k_5 = 0$, in accordance with (51).

Though the physical meaning of the fifth coordinate is not yet quite clear [26]), the formal simplification to which it leads is striking.

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[26]) Though of course it may be interpreted in one of the well-known ways. Cf. the references, given in EM1, p. 522, note [2]).